# The Differential Equations of Thermodynamics

Second Edition, Revised

V. V. Sychev


ИЗДАТЕЛЬСТВО
МИР

В. В. СЫЧЁВ

# ДИФФЕРЕНЦИАЛЬНЫЕ УРАВНЕНИЯ ТЕРМОДИНАМИКИ

ИЗДАТЕЛЬСТВО «НАУКА»
МОСКВА

# The Differential Equations of Thermodynamics

## V. V. Sychev

*Translated from the Russian*
*by Eugene Yankovsky*

ERRATUM

p. 124, formula (5.162) instead of $\left(\frac{Tp}{\partial v}\right)_s$ read $\left(\frac{\partial T}{\partial v}\right)_s$

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## To the Reader

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# Preface
# to the Russian Edition

Thermodynamics, as is known, is constructed quite simply. Two of its main laws have been established experimentally, and by applying mathematical tools to them we can obtain the range of conclusions in which thermodynamics is so rich.

The mathematical tools of thermodynamics are simple but in certain aspects at the same time quite sophisticated. Neglecting some of these sophisticated "trifles" often results in crude mistakes, even in reputable works on thermodynamics.

The restricted size of the usual textbooks on thermodynamics does not permit discussing more extensively these important questions concerning the mathematical tools. For this reason it was felt necessary to consider these problems in a special book, which though limited in size would at the same time go into details.

Naturally, the author does not aim at a presentation of thermodynamics and its physical, chemical, and technical applications. These have been sufficiently discussed in the existing textbooks and monographs. The purpose of this book is more modest—to deepen the reader's knowledge of the mathematical tools of thermodynamics, to systematize them, and at the same time to emphasize questions that are often a source of error in thermodynamic calculations. The book is therefore designed to meet the needs of students and graduates majoring in thermal physics, physical engineering, and physico-technical specialities who already have a background in general thermodynamics. I hope that the book may also prove useful to scientists, engineers, and teachers specializing in thermodynamics.

Comments on the contents of this book will be much appreciated.

*V.V. Sychev*

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# 1 Recollections of Thermodynamics: A Survey Chapter

This book considers the mathematical tools of thermodynamics and its applications. It is not intended to give a detailed analysis of the general problems of thermodynamics. Therefore, in this chapter we briefly discuss some concepts of thermodynamics necessary for subsequent presentation.

## 1.1 Basic Concepts of Thermodynamics

1.1.1. The thermodynamic quantities characterizing a substance are either intensive or extensive.

Intensive quantities are those whose values do not depend on the amount of substance in the system (pressure, temperature, and some others).

Extensive quantities are those whose values depend on the amount of substance in the system. Volume, which varies under given conditions with the amount of substance, can serve as an example of an extensive quantity.

Specific extensive quantities, i.e. the values per unit amount of substance, behave like intensive quantities.

Intensive quantities that determine the state of a body or group of bodies (a thermodynamic system) are called *thermodynamic parameters* of the state of the body (system). The most convenient and, therefore, the most widespread parameters of state are temperature, pressure, and specific volume (density) of the body.

When no external forces act on the system, the state of a pure substance is uniquely determined if two intensive independent parameters are given. (When we have a mixture of substances and when a system is under external forces, e.g. an external electric field or external magnetic field, the number of parameters necessary to determine uniquely the state of the system increases. In this book we will deal only with pure substances.) Any other parameter is a function of two given parameters. Hence, any three parameters of state (e.g. pressure $p$, specific volume $v$, and temperature $T$) of a pure substance are uniquely related to each other. The equation that connects any three parameters is called the *equation of state* for a given substance. For each substance the relationship between these parameters is individual and, hence, thermodynamic properties are described by an equation of state specifically for each substance.

The relationship between the parameters of state can be represented by the so-called *state surface* in a system of coordinates (e.g. $p$, $v$, $T$) along whose axes the values of these parameters are laid off. The projections of this thermodynamic surface on the coordinate planes (say $p$-$v$, $p$-$T$, or $v$-$T$ planes) are called phase diagrams of the substance.

1.1.2. By a thermodynamic system we understand a collection of bodies interacting with each other and the surrounding medium; all other bodies beyond the boundaries of the system are called the surrounding medium.

If at least one of the state parameters of the system changes, the state of the system changes, too, i.e. a thermodynamic process takes place. This process is a collection of varying states of the system under consideration.

1.1.3. Thermodynamic quantities can be divided into two categories: process functions and state functions.

Thermodynamic quantities whose values (with the state of the system varying in the course of thermodynamic process from initial state *1* to terminal state *2*) depend on the path of the process *1-2* are termed process functions. In other words, if $\nu$ is a process function, the amount by which this function changes in the process *1-2*, $\nu_{1-2}$, defined by the obvious relation

$$\nu_{1-2}=\int\limits_{(1-2)} d\nu, \tag{1.1}$$

will differ depending on the path along which the line integral (1.1) is calculated. As is known from thermodynamics, heat and work are process functions.

Thermodynamic quantities whose values (with the state of the system varying in the course of a thermodynamic process from initial state *1* to terminal state *2*) do not depend on what path the process *1-2* takes and are defined only by the difference of the values of the given function in the terminal and initial states, are termed state functions. In other words, if $\mu$ is a state function,

$$\int\limits_{(1-2)} d\mu=\int\limits_{1}^{2} d\mu=\mu_2-\mu_1. \tag{1.2}$$

Internal energy, enthalpy, and entropy are examples of state functions.

1.1.4. Thermodynamic systems can perform different types of work: the work of expansion against external pressure, the work of increasing a surface area against surface tension, the work of displacing a body in a gravitational field, the work of polarizing dielectrics in an electric field, and so on. We know that although all these types of work differ greatly there is a common formula for calculating the work $L$:

$$dL = \zeta\, dY. \tag{1.3}$$

Here $\zeta$ is the external force acting on the body (system), and $Y$ is the state parameter (coordinate) of the system conjugate to the force $\zeta$. It is common practice to call $\zeta$ a *generalized force* and $Y$ a *generalized coordinate*.[1]

If a system performs work against external pressure $p$ accompanied by an increase in volume $V$ (the so-called work of expansion), then (1.3) becomes

$$dL = p\, dV. \tag{1.4}$$

It should be noted that different types of generalized force have different generalized coordinates conjugate to them. When considering particular systems we will always establish what state parameter of the system is a generalized force and what a generalized coordinate.

If several types of force act simultaneously on a system, then evidently the work done by the system is the sum of the amount of work done by the system under the action of each force:

$$dL = \sum_{i=1}^{n} \zeta_i\, dY_i, \tag{1.5}$$

where $\zeta_i$ is the $i$th generalized force, and $Y_i$ the generalized coordinate conjugate to this force; $n$ the number of generalized forces.

Thermodynamic systems performing only work of expansion will be called simple systems, while those performing other work besides work of expansion complex systems.

In what follows we will consider systems performing either only work of expansion (i.e. simple systems) or performing no more than two types of work simultaneously, one being work of expansion. It is therefore expedient to represent the work $L$ done by the complex system as a sum of two terms: the work of expansion and any other possible type of work. Let us denote by $L^*$ any type of work other than expansion work $p\, dV$. Then, obviously,

$$dL = p\, dV + dL^*. \tag{1.6}$$

---

[1] Sometimes in the literature a generalized force is called an intensity factor and a generalized coordinate a capacity factor. These names indicate that generalized forces are intensive quantities and generalized coordinates extensive.

We will also use the notations

$$dL^* = \xi\, dW, \tag{1.7}$$

where $\xi$ is a generalized force with the exception of pressure, and $W$ is a generalized coordinate with the exception of volume. In accordance with these notations Eq. (1.6) can be written thus:

$$dL = p\, dY + \xi\, dW. \tag{1.8}$$

Obviously, for mass specific values (i.e. per unit mass) of the thermodynamic quantities in Eqs. (1.3) through (1.8) these equations can be written thus:

$$dl = \zeta\, dy, \tag{1.3a}$$

$$dl = p\, dv, \tag{1.4a}$$

$$dl = \sum_{i=1}^{n} \zeta_i\, dy_i, \tag{1.5a}$$

$$dl = p\, dv + dl^*, \tag{1.6a}$$

$$dl = \xi\, dw, \tag{1.7a}$$

$$dl = p\, dv + \xi\, dw; \tag{1.8a}$$

where $v$ is the specific volume, and $y$ and $w$ the mass specific values of the generalized coordinates $Y$ and $W$ ($y = Y/G$ and $w = W/G$, with $G$ the mass of the substance in the system).

## 1.2 The Equations of the First and Second Laws of Thermodynamics

1.2.1. We know that the equation of the first law of thermodynamics, the law of conservation and conversion of energy, can be written in the following form:

$$dQ = dU + dL, \tag{1.9}$$

where $Q$ is the amount of heat supplied to or rejected from a thermodynamic system, $U$ the internal energy of the system, and $L$ the work done by the system (or done on the system).

We noted above that neither $Q$ nor $L$ is a state function; both depend on the process by which the system goes from state *1* to state *2*. So $dQ$ and $dL$, are, obviously, not total differentials.

For simple systems Eq. (1.9) combined with (1.4) is written

$$dQ = dU + p\, dV, \tag{1.10}$$

while for complex systems, using (1.5), (1.6), and (1.8), respectively,

$$dQ = dU + \sum_{i=1}^{n} \zeta_i \, dY_i, \tag{1.11}$$

$$dQ = dU + p\,dV + dL^*, \tag{1.12}$$

and

$$dQ = dU + p\,dY + \xi\,dW. \tag{1.13}$$

In the same way, for mass specific values of thermodynamic quantities these relationships are written thus:

$$dq = du + p\,dv, \tag{1.10a}$$

$$dq = du + \sum_{i=1}^{n} \zeta_i \, dy_i, \tag{1.11a}$$

$$dq = du + p\,dv + dl^*, \tag{1.12a}$$

$$dq = du + p\,dv + \xi\,dw. \tag{1.13a}$$

1.2.2. Enthalpy is one of the most important thermodynamic quantities. For simple systems enthalpy $H$ is determined by the following relation:

$$H = U + pV, \tag{1.14}$$

while for complex systems by the relation

$$H^* = U + pV + \xi W. \tag{1.15}$$

In the same way specific enthalpy for simple systems is

$$h = u + pv, \tag{1.14a}$$

and for complex systems

$$h^* = u + pv + \xi w. \tag{1.15a}$$

1.2.3. The equation of the first law of thermodynamics for a stationary flow of a liquid or gas in a channel can be written in terms of (mass) specific quantities as

$$dq = dh + w\,dw + g\,dz + dl_{\text{tech}} + dl_{\text{diss}}, \tag{1.16}$$

where $q$ is the heat supplied to the flow (or rejected from it), $h$ the enthalpy of the fluid, $w$ the flow velocity, $z$ the height, $l_{\text{tech}}$ the so-called technical work done by the flow, $l_{\text{diss}}$ the dissipative work (e.g. the work done by the flow in overcoming frictional forces), and $g$ the acceleration of gravity.

The heat $q$ in Eq. (1.16) consists of two parts: the heat $q_{\text{ext}}$ brought into the flow from outside (or rejected from it to the surroundings) and the dissipative heat $q_{\text{diss}}$, liberated, for instance, when the flow involves friction:

$$q = q_{\text{ext}} + q_{\text{diss}}. \tag{1.17}$$

Since $q_{\text{diss}}$ is equivalent to $l_{\text{diss}}$, we can write Eq. (1.16) in the following form:

$$dq_{\text{ext}} = dh + w\,dw + g\,dz + dl_{\text{tech}}; \tag{1.18}$$

the equation is valid both with and without friction in the flow.

1.2.4. An analytic expression for the second law of thermodynamics has the form

$$T\,dS \geqslant dQ, \tag{1.19}$$

with $S$ the entropy of the system. In terms of specific quantities this relation is

$$T\,ds \geqslant dq. \tag{1.19a}$$

Here the "greater than" sign is used when the system undergoes an irreversible process, and the equality holds when the process is reversible.

Hence, for reversible processes

$$dQ = T\,dS \tag{1.20}$$

and, respectively,

$$dq = T\,ds. \tag{1.20a}$$

1.2.5. From Eqs. (1.9) and (1.19) we can see that a combined equation for the first and second laws of thermodynamics can be written as

$$T\,dS \geqslant dU + dL. \tag{1.21}$$

For a simple system this relation together with (1.4) is transformed thus:

$$T\,dS \geqslant dU + p\,dV, \tag{1.22}$$

whereas for a complex system Eq. (1.21) combined with (1.5) yields

$$T\,dS \geqslant dU + \sum_{i=1}^{n} \zeta_i\,dY_i, \tag{1.23}$$

or, which is the same, combining (1.21) with (1.6), we obtain

$$T\,dS \geqslant dU + p\,dV + dL^*; \tag{1.24}$$

for a complex system performing one more type of work besides work of expansion we can employ (1.7) and write

$$T\,dS \geqslant dU + p\,dV + \xi\,dW. \tag{1.25}$$

In accordance with the above, when a system undergoes reversible processes, relations (1.21) through (1.25) have the form:

for all systems

$$T\,dS = dU + dL, \tag{1.26}$$

for a simple system

$$T\,dS = dU + p\,dV, \tag{1.27}$$

and for a complex system

$$T\,dS = dU + \sum_{i=1}^{n} \zeta_i\,dY_i, \tag{1.28}$$

$$T\,dS = dU + p\,dV + dL^*, \tag{1.29}$$

$$T\,dS = dU + p\,dV + \xi\,dW. \tag{1.30}$$

Obviously, for mass specific values of thermodynamic quantities Eqs. (1.21) through (1.25) are respectively written in the following form:

$$T\,ds \geqslant du + dl, \tag{1.21a}$$

$$T\,ds \geqslant du + p\,dv, \tag{1.22a}$$

$$T\,ds \geqslant du + \sum_{i=1}^{n} \zeta_i\,dy_i, \tag{1.23a}$$

$$T\,ds \geqslant du + p\,dv + dl^*, \tag{1.24a}$$

$$T\,ds \geqslant du + p\,dv + \xi\,dw, \tag{1.25a}$$

and Eqs. (1.26) through (1.30) in the following form:

$$T\,ds = du + dl, \tag{1.26a}$$

$$T\,ds = du + p\,dv, \tag{1.27a}$$

$$T\,ds = du + \sum_{i=1}^{n} \zeta_i\,dy_i, \tag{1.28a}$$

$$T\,ds = du + p\,dv + dl^*. \tag{1.29a}$$

$$T\,ds = du + p\,dv + \xi\,dw. \tag{1.30a}$$

1.2.6. These are the basic thermodynamic relationships that we will need in what follows.

# 2 The Mathematical Tools of Thermodynamics

## 2.1 Derivatives of Functions of Several Variables

2.1.1. Thermodynamics deals mainly with functions of several variables. The following notation is assumed in thermodynamics: a partial derivative of a function $z\ (x_1, \ldots, x_n)$ with respect to the variable $x_i$ is denoted by $(\partial z/\partial x_i)_{x \neq x_i}$; here the subscript indicates that the derivative is taken assuming that the quantity in the subscript is constant. For instance, the derivative of pressure with respect to temperature, $\partial p/\partial T$, showing how the pressure varies with temperature, may be calculated in various conditions: at constant volume $V$, at constant entropy $S$, at constant enthalpy $H$, and so on. In each case the derivative is denoted by $(\partial p/\partial T)_V$, $(\partial p/\partial T)_S$, or $(\partial p/\partial T)_H$ and differs in value.

The well-known relationships for the derivatives of functions of several variables are widely used when considering differential equations of thermodynamics. These relationships are given below in Secs. 2.1.2 through 2.1.5.

As a rule, we will consider thermodynamic quantities that are functions of two variables.[1] It may happen that one of the variables is a unique function of another variable.

If a variable $y$ is uniquely related to $x$ and, therefore, $y = y\ (x)$, the function $z\ (x, y)$ is, in the final analysis, a function of one variable; consequently, $\partial z/\partial x$ is a total derivative, $dz/dx$. For instance, the specific volume of a pure substance $v$ is in general a function of two thermodynamic parameters (e.g. pressure $p$ and temperature $T$). However, the specific volume of a substance, $v_\sigma$, on a boundary curve separating a one-phase region from a two-phase region is a function of only one variable, since, as we know, the pressure in a saturated state is uniquely related to temperature. Hence, in connection with the specific volume on the boundary curve we can say that the derivative of $v$ with respect to $T$ along this curve is a total rather than a partial derivative, $dv_\sigma/dT$. Therefore, below (Chaps. 6 through 9) we will deal with both partial and total derivatives of thermodynamic quantities.

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[1] Cases where a thermodynamic quantity is a function of more than two variables will be stipulated.

2.1.2. We will often use the well-known relations for partial derivatives

$$\left(\frac{\partial y}{\partial x}\right)_z = 1 \bigg/ \left(\frac{\partial x}{\partial y}\right)_z \tag{2.1}$$

and for total derivatives

$$\frac{dy}{dx} = 1 \bigg/ \frac{dx}{dy} \tag{2.2}$$

(these relations are also known as the theorem on inverse quantities) For instance,

$$\left(\frac{\partial p}{\partial T}\right)_v = 1 \bigg/ \left(\frac{\partial T}{\partial p}\right)_v, \tag{2.3}$$

and on the saturation line

$$\frac{dp}{dT} = 1 \bigg/ \frac{dT}{dp}. \tag{2.4}$$

2.1.3. We will examine differentiation of a composite function. If $y = y(u)$, and, in its turn, $u = u(x_1, \ldots, x_n)$ and, hence, $y = y(x_1, \ldots, x_n)$, then, as we know, the following relationship (the so-called chain rule) holds:

$$\left(\frac{\partial y}{\partial x_i}\right)_{x \neq x_i} = \left(\frac{\partial y}{\partial u}\right)_{x \neq x_i} \left(\frac{\partial u}{\partial x_i}\right)_{x \neq x_i}. \tag{2.5}$$

For the case of two variables, where $y = y(x, z)$ and $u = u(x, z)$, this relationship is

$$\left(\frac{\partial y}{\partial x}\right)_z = \left(\frac{\partial y}{\partial u}\right)_z \left(\frac{\partial u}{\partial x}\right)_z. \tag{2.6}$$

For instance, the chain rule enables us to write

$$\left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{\partial p}{\partial s}\right)_v \left(\frac{\partial s}{\partial T}\right)_v; \tag{2.7}$$

obviously, here $p = p(T, v)$ and $s = s(T, v)$.

In a similar manner, if we take a function of one variable, $y = y(u)$, and $u = u(x)$, then

$$\frac{dy}{dx} = \frac{dy}{du}\frac{du}{dx}. \tag{2.8}$$

For example, along the boundary curve

$$\frac{dp}{dT} = \frac{dp}{dv}\frac{dv}{dT}. \tag{2.9}$$

Using (2.1) and (2.2), we can write (2.6) and (2.8), respectively, in the following form:

$$\left(\frac{\partial y}{\partial x}\right)_z \left(\frac{\partial x}{\partial u}\right)_z \left(\frac{\partial u}{\partial y}\right)_z = 1 \tag{2.10}$$

and

$$\frac{dy}{dx}\frac{dx}{du}\frac{du}{dy} = 1. \tag{2.11}$$

2.1.4. When deriving important equations of thermodynamics, we make use of the Bernoulli-Euler theorem on the equality of mixed second-order derivatives, which states that if the mixed second-order derivatives of a function $z\ (x,\ y)$ are continuous at point $P\ (x,\ y)$, then they are equal at this point. In other words, for the function $z\ (x,\ y)$ the value of its mixed second-order derivative does not depend on the order of differentiation:

$$\frac{\partial^2 z}{\partial x\, \partial y} = \frac{\partial^2 z}{\partial y\, \partial x}, \tag{2.12}$$

or, which is the same,

$$\left[\frac{\partial}{\partial y}\left(\frac{\partial z}{\partial x}\right)_y\right]_x = \left[\frac{\partial}{\partial x}\left(\frac{\partial z}{\partial y}\right)_x\right]_y. \tag{2.13}$$

2.1.5. The relation between second derivatives $d^2y/dx^2$ and $d^2x/dy^2$ is often used in thermodynamic equations. We see from (2.2) that

$$\frac{d^2y}{dx^2} = \frac{d}{dx}\left(\frac{dx}{dy}\right)^{-1}. \tag{2.14}$$

The right-hand side of the relation combined with (2.8) may be transformed to the following form:

$$\frac{d}{dx}\left(\frac{dx}{dy}\right)^{-1} = \frac{d}{dy}\left(\frac{dx}{dy}\right)^{-1}\frac{dy}{dx}, \tag{2.15}$$

whence

$$\frac{d}{dx}\left(\frac{dx}{dy}\right)^{-1} = -\frac{d^2x}{dy^2}\left(\frac{dy}{dx}\right)^3 \tag{2.16}$$

and, consequently,

$$\frac{d^2y}{dx^2} = -\frac{d^2x}{dy^2}\left(\frac{dy}{dx}\right)^3. \tag{2.17}$$

In the same manner we can show that

$$\left(\frac{\partial^2 y}{\partial x^2}\right)_z = -\left(\frac{\partial^2 x}{\partial y^2}\right)_z\left(\frac{\partial y}{\partial x}\right)_z^3. \tag{2.18}$$

2.1.6. These are some mathematical relations generally used in the differential equations of thermodynamics.

## 2.2 Pfaffian Forms and Total Differentials

2.2.1. Differential relationships used in thermodynamics, such as those considered in Chap. 1 (the equation of the first law of thermodynamics, the combined equation for the first and second laws of thermodynamics, the relations for the work of a thermodynamic system, and the expressions for differentials of various thermodynamic functions), are similar in structure and have the form

$$dZ = A_1(x_1, \ldots, x_n)\, dx_1 + \ldots + A_n(x_1, \ldots, x_n)\, dx_n, \tag{2.19}$$

where $x_1, \ldots, x_n$ are variables. The expression on the right-hand side,

$$\sum_{i=1}^{n} A_i(x_1, \ldots, x_n)\, dx_i, \tag{2.20}$$

is called a *Pfaffian differential expression* or a *Pfaffian form.*

Obviously, the equation of the first law of thermodynamics for simple systems, (1.10), is a Pfaffian form in two variables; for systems performing one more type of work besides work of expansion, (1.13) is the Pfaffian form in three variables; finally, for systems performing $n$ types of work, (1.11) is a Pfaffian form in $(n+1)$ variables.

We know that the total differential of a function of several (independent) variables, $z = z(x_1, \ldots, x_n)$, is defined as

$$dz = \sum_{i=1}^{n} \left(\frac{\partial z}{\partial x_i}\right)_{x \neq x_i} dx_i. \tag{2.21}$$

This is, obviously, a particular case of Eq. (2.19); here

$$A_i(x_1, \ldots, x_n) = \left(\frac{\partial z}{\partial x_i}\right)_{x \neq x_i}. \tag{2.22}$$

In the majority of cases we will consider functions of two variables and, therefore, deal with differential relations of the form

$$dZ = M(x, y)\, dx + N(x, y)\, dy \tag{2.23}$$

and total differentials of the form

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy. \tag{2.24}$$

2.2.2. The most important question concerning thermodynamic relations of the type (2.19) or (2.23) is whether the Pfaffian form in the right-hand side of these relations is a total differential of $Z$. The point is that if $dZ$ is a total differential, the variation of $Z$ when we move from point *1* $(x_1, y_1)$ on the state surface to point

*2* $(x_2, y_2)$ is given simply by the difference between the values of $Z$ at these points:

$$\int_1^2 dZ = Z_2 - Z_1. \tag{2.25}$$

If $dZ$ is not a total differential, the variation of $Z$ when we move from point *1* $(x_1, y_1)$ to point *2* $(x_2, y_2)$,

$$\Delta Z_{1\text{-}2} = \int\limits_{(1\text{-}2)} dZ, \tag{2.26}$$

is different depending on the path.

As we noted in Sec. 1.1.3, thermodynamic quantities are divided into two categories: state functions and process functions. From the aforesaid it is obvious that a special feature of a state function is that its differential is total, while for a process function its differential is not total.

It is very important to find a criterion which will enable us to determine uniquely whether a given Pfaffian form in an equation of the type (2.19) or (2.23) is a total differential. Such a criterion was found by L. Euler.

If the Pfaffian form

$$M(x, y)\, dx + N(x, y)\, dy \tag{2.27}$$

is a total differential, then, as noted above (see (2.22)),

$$M = \left(\frac{\partial Z}{\partial x}\right)_y \tag{2.28}$$

and

$$N = \left(\frac{\partial Z}{\partial y}\right)_x. \tag{2.29}$$

Since, according to the Bernoulli-Euler theorem, for the function $Z(x, y)$ the value of its mixed second-order derivative does not depend on the order of differentiation (see Eq. (2.12)),

$$\frac{\partial^2 Z}{\partial x\, \partial y} = \frac{\partial^2 Z}{\partial y\, \partial x},$$

from (2.28) and (2.29) it follows that

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y. \tag{2.30}$$

This implies that if condition (2.30) is met for a differential relation of the type (2.32), then $dZ$ is a total differential and, hence, $Z$ is a state function. But if condition (2.30) is not met, i.e. $(\partial M/\partial y)_x \neq$

$\neq (\partial N/\partial x)_y$, the Pfaffian form on the right-hand side of (2.24) is not a total differential and $Z$ is a process function.

The Euler condition (2.30) is an important mathematical tool of thermodynamics. For instance, it enables showing that the differential of an amount of heat is not total.

Let us consider the equation of the first law of thermodynamics for a simple system (1.10):

$$dQ = dU + p\,dV.$$

The above relationship implies that $Q$ is a function of $U$ and $V$. According to the notations of Eq. (2.23), $M = 1$, $x = U$, $N = p$, and $y = V$. Hence,

$$\left(\frac{\partial M}{\partial y}\right)_x = 0 \tag{2.31}$$

and

$$\left(\frac{\partial N}{\partial x}\right)_y = \left(\frac{\partial p}{\partial U}\right)_V. \tag{2.32}$$

In its turn,

$$\left(\frac{\partial p}{\partial U}\right)_v = \left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial T}{\partial U}\right)_V, \tag{2.33}$$

i.e.

$$\left(\frac{\partial N}{\partial x}\right)_y = \frac{1}{C_V} \left(\frac{\partial p}{\partial T}\right)_V, \tag{2.34}$$

where $C_V = (\partial U/\partial T)_V$ is the total heat capacity of the system. Since (2.31) differs from (2.34), the differential $dQ$ is not total and $Q$ is a process function.

In the same manner we can show that the differential of work is not total. Take the work of expansion, for instance. Since here $L$ is a function of two variables, pressure $p$ and volume $V$, for the differential of this function we may generally write

$$dL = M\,dp + N\,dV. \tag{2.35}$$

But since by (1.4)

$$dL = p\,dV,$$

according to the notations of (2.23) we can write $M = 1$, $x = p$, $N = p$, and $y = V$; therefore,

$$\left(\frac{\partial M}{\partial y}\right)_x = 0, \tag{2.36}$$

$$\left(\frac{\partial N}{\partial x}\right)_y = 1. \tag{2.37}$$

We see that the quantities $(\partial M/\partial y)_x$ and $(\partial N/\partial x)_y$ are different and the differential $dL$ is not total.

In the same manner we can show that for a function of three variables

$$dZ = M\,dx + N\,dy + P\,du. \tag{2.38}$$

and the Euler condition will have the following form: since

$$M = \left(\frac{\partial Z}{\partial x}\right)_{y,u}, \tag{2.39}$$

$$N = \left(\frac{\partial Z}{\partial y}\right)_{x,u}, \tag{2.40}$$

$$P = \left(\frac{\partial Z}{\partial u}\right)_{x,y}, \tag{2.41}$$

we find that

$$\left(\frac{\partial M}{\partial y}\right)_{x,u} = \left(\frac{\partial N}{\partial x}\right)_{y,u}, \tag{2.42}$$

$$\left(\frac{\partial N}{\partial u}\right)_{x,y} = \left(\frac{\partial P}{\partial y}\right)_{x,u}, \tag{2.43}$$

$$\left(\frac{\partial M}{\partial u}\right)_{x,y} = \left(\frac{\partial P}{\partial x}\right)_{y,u}. \tag{2.44}$$

Conditions (2.42) through (2.44) may be represented in a brief form

$$\operatorname{curl} \mathbf{R} = 0, \tag{2.45}$$

where **R** is a vector with components $M$, $N$, and $P$.

In the general case of $n$ variables the Pfaffian form (2.20) is a total differential if and only if for all $i$ and $k$ the following conditions are met:

$$\frac{\partial A_i}{\partial x_k} = \frac{\partial A_k}{\partial x_i}; \tag{2.46}$$

by analogy with (2.45) we can write these conditions in tensor form.

2.2.3. When differential (2.23) is not total, i.e. condition (2.30) is not met, one would like to transform (2.23) so that it (or a proportional expression) becomes a total differential. From mathematical analysis we know that there exists a function $\lambda\,(x,\ y)$ such that by multiplying it by the Pfaffian form (2.23) we obtain the total differential of a function $R\,(x,\ y)$. The function $\lambda\,(x,\ y)$ is termed an integrating factor. From this it follows that if $\lambda$ is an integrating factor for the Pfaffian form

$$dZ = M\,dx + N\,dy,$$

then

$$\lambda M\,dx + \lambda N\,dy = dR, \tag{2.47}$$

where

$$\lambda M = \left(\frac{\partial R}{\partial x}\right)_y \tag{2.48}$$

and

$$\lambda N = \left(\frac{\partial R}{\partial y}\right)_x . \tag{2.49}$$

Whence

$$\left(\frac{\partial \lambda M}{\partial y}\right)_x = \left(\frac{\partial \lambda N}{\partial x}\right)_y , \tag{2.50}$$

or

$$N\left(\frac{\partial \lambda}{\partial x}\right)_y - M\left(\frac{\partial \lambda}{\partial y}\right)_x = \left[\left(\frac{\partial M}{\partial y}\right)_x + \left(\frac{\partial N}{\partial x}\right)_y\right]\lambda, \tag{2.51}$$

i.e.

$$N\left(\frac{\partial \ln \lambda}{\partial x}\right)_y - M\left(\frac{\partial \ln \lambda}{\partial y}\right)_x = \left(\frac{\partial M}{\partial y}\right)_x - \left(\frac{\partial N}{\partial x}\right)_y . \tag{2.52}$$

This equation yields the sought quantity $\lambda\ (x,\ y)$.

We can also show that any function of type

$$\lambda_1 = \lambda f\ (R) \tag{2.53}$$

is also an integrating factor. In fact, the number of integrating factors is infinite (since we may construct an infinitude of functions of the $\lambda_1$ type).

Thus we have considered two types of Pfaffian forms: (a) Pfaffian forms that are total differentials, and (b) Pfaffian forms that are not total differentials but are proportional to such, i.e. have an integrating factor transforming the Pfaffian form into the total differential of a function $R\ (x,\ y)$.

Moreover, there is a third type of Pfaffian form. These are not total differentials and have no integrating factor.

It is customary to call Pfaffian forms of the second type (with integrating factors) holonomic and Pfaffian forms of the third type (without integrating factors) nonholonomic.

According to Cauchy's theorem, a Pfaffian form in two variables is always holonomic, which follows from Eqs. (2.47) through (2.52).

As for Pfaffian forms in three and more variables, some are holonomic while others are not. For one, a Pfaffian form in three variables,

$$M\,dx + N\,dy + P\,du, \tag{2.54}$$

may be holonomic or nonholonomic. As is shown in mathematical analysis, a Pfaffian form in three variables is holonomic if the following relationship[2] is valid:

$$M\left[\left(\frac{\partial M}{\partial u}\right)_{x,y}-\left(\frac{\partial P}{\partial y}\right)_{x,u}\right]+N\left[\left(\frac{\partial P}{\partial x}\right)_{y,u}-\left(\frac{\partial M}{\partial u}\right)_{x,y}\right]$$
$$+P\left[\left(\frac{\partial M}{\partial y}\right)_{x,u}-\left(\frac{\partial N}{\partial x}\right)_{y,u}\right]=0. \tag{2.55}$$

It should be noted that the problem of holonomic and nonholonomic Pfaffian forms in three and more variables is of great interest to thermodynamics. Although this problem is not directly connected with the main subject of the book, we think it expedient to consider it at least briefly.

Starting with the second law of thermodynamics in its traditional form (formulated by R. J. Clausius), we can introduce the concept of entropy via the relation

$$dS=\frac{1}{T}dQ. \tag{2.57}$$

Entropy is a state function and, therefore, its differential is total, unlike $dQ$. This means that the quantity $1/T$ is an integrating factor for the Pfaffian form $dQ$.

Taking this fact into account, C. Carathéodory in 1909 suggested a statement of the second law of thermodynamics alternative to the traditional (Clausius) statement. Carathéodory confirmed that there exists an integrating factor for the Pfaffian form $dQ$ ("the Pfaffian form $dQ$ is holonomic"). He formulated the following criterion for the existence of an integrating factor for Pfaffian forms in more than two variables: a Pfaffian form $dQ$ has an integrating factor if and only if arbitrarily close to a given point (in a space of variables whose function the Pfaffian form is) there are points that can not be attained by moving from the given point along the surface $dQ = 0$.

The meaning of this statement is as follows. The differential equation of the type

$$\sum_{i=1}^{n} A_i dx_i = 0 \tag{2.58}$$

---

[2] This relation can be written in vector form

$$\mathbf{R}\cdot\operatorname{curl}\mathbf{R} = 0, \tag{2.56}$$

with notations the same as in (2.45).

is known as the Pfaffian equation. If the Pfaffian form on the left-hand side of this equation is holonomic, the equation can be transformed into

$$dR = 0, \tag{2.59}$$

where

$$dR(x_1, \ldots, x_n) = \lambda(x_1, \ldots, x_n) \sum_{i=1}^{n} A_i \, dx_i. \tag{2.60}$$

Since $dR$ is a total differential, (2.59) has solutions

$$R(x_1, \ldots, x_n) = C, \tag{2.61}$$

where $C$ is a constant (it is obvious that there is an infinitude of such constants). Here (2.61) is the equation of a surface in $n$-dimensional space and, therefore, there is a family of surfaces corresponding to the solutions of this equation.

From the standpoint of the Pfaffian form $dQ$, Eq. (2.58) corresponds to an adiabatic system

$$dQ = 0. \tag{2.62}$$

This explains why the surfaces (2.62) given by the solution of the Pfaffian equation are termed adiabatic surfaces. Carathéodory postulated that these surfaces do not intersect. But if this is the case, then, obviously, a point $(x_1, \ldots, x_n)$ corresponding to a definite state of the thermodynamic system can belong to only one adiabatic surface. Consequently, arbitrarily close to the considered state there are other states (points belonging to other adiabatic surfaces) that cannot be attained by moving along an adiabatic path from the given point. This statement (the principle of adiabatic inaccessibility) constitutes the main point of Carathéodory's formulation of the second law of thermodynamics: "In the immediate neighbourhood of each state of a system there are other states which cannot be attained by an adiabatic path alone."

The meaning of this statement is clear, since it is easy to show that the converse is also true: if arbitrarily close to the given state there are other states inaccessible by an adiabatic path, then, consequently, the Pfaffian form $dQ$ is holonomic. Thus, if the principle of adiabatic inaccessibility is true, $dQ$ is holonomic; as Carathéodory showed, from the fact that $dQ$ is holonomic follows the existence of entropy of thermodynamic systems.

In considering Carathéodory's theory we must clearly understand the following point. We know that the second law of thermodynamics was formulated on the basis of data accumulated as a result of direct observations of macrosystems; this fact is included in the traditional formulation of the second law of thermodynamics (the Clausius postulate, which states that heat cannot transfer by itself from the cold body to the hot). It might seem that Carathéodory formulated the second law of thermodynamics purely theoretically without employing experimental data (i.e. not postulating but "proving" the law). Actually this is not true: the principle of adiabatic inaccessibility is a postulate (i.e. a hypothesis assumed without proof) to the same extent as the above mentioned Clausius postulate; in fact, Carathéodory's principle in the final analysis postulates the unprovable proposition that the Pfaffian form $dQ$ in $n$ variables is always holonomic.

## 2.3 The Relationships Between Derivatives

2.3.1. The expression for the total differential of a function $z\ (x,\ y)$

$$dz = M\,dx + N\,dy, \quad . \tag{2.63}$$

where $M = (\partial z/\partial x)_y$ and $N = (\partial z/\partial y)_x$, clearly shows that

$$\left(\frac{\partial z}{\partial m}\right)_n = M\left(\frac{\partial x}{\partial m}\right)_n + N\left(\frac{\partial y}{\partial m}\right)_n. \tag{2.64}$$

This relationship is often used in thermodynamics. For instance, from Eq. (1.27a)

$$T\,ds = du + p\,dv$$

combined with (2.64) it follows that

$$T\left(\frac{\partial s}{\partial p}\right)_T = \left(\frac{\partial u}{\partial p}\right)_T + p\left(\frac{\partial v}{\partial p}\right)_T. \tag{2.65}$$

It is clear that since $M = (\partial z/\partial x)_y$ and $N = (\partial z/\partial y)_x$, Eq. (2.64) can also be written in the following form:

$$\left(\frac{\partial z}{\partial m}\right)_n = \left(\frac{\partial z}{\partial x}\right)_y\left(\frac{\partial x}{\partial m}\right)_n + \left(\frac{\partial z}{\partial y}\right)_x\left(\frac{\partial y}{\partial m}\right)_n. \tag{2.66}$$

If we put $m = x$ and $n = z$, we find that

$$\left(\frac{\partial z}{\partial x}\right)_y\left(\frac{\partial x}{\partial y}\right)_z\left(\frac{\partial y}{\partial z}\right)_x = -1. \tag{2.67}$$

Obviously, if a quantity $z$ is a function of two variables $x$ and $y$, or $z = z\ (x,\ y)$, we are justified in considering $x$ as a function of $y$ and $z$, or $x = x\ (y,\ z)$, and $y$ as a function of $x$ and $z$, or $y = y\ (x,\ z)$. Equation (2.67) uniquely relates all possible derivatives of these three functions.

This equation (a linkage of three derivatives) is widely used in thermodynamics. According to (2.67), for $p$, $v$, and $T$ we have

$$\left(\frac{\partial p}{\partial T}\right)_v\left(\frac{\partial T}{\partial v}\right)_p\left(\frac{\partial v}{\partial p}\right)_T = -1, \tag{2.68}$$

for $h$, $u$, and $s$

$$\left(\frac{\partial h}{\partial s}\right)_u\left(\frac{\partial s}{\partial u}\right)_h\left(\frac{\partial u}{\partial h}\right)_s=-1, \tag{2.69}$$

and for $p$, $s$, and $v$

$$\left(\frac{\partial p}{\partial v}\right)_s\left(\frac{\partial v}{\partial s}\right)_p\left(\frac{\partial s}{\partial p}\right)_v=-1. \tag{2.70}$$

2.3.2. If we set $m=x$ but $n\neq z$, then from (2.66) there follows one more useful relationship:

$$\left(\frac{\partial z}{\partial x}\right)_m=\left(\frac{\partial z}{\partial x}\right)_y+\left(\frac{\partial z}{\partial y}\right)_x\left(\frac{\partial y}{\partial x}\right)_m. \tag{2.71}$$

This equation can be used to relate the partial derivatives of given quantities that have been calculated with different constant parameters. For instance, if we wish to find the relation between the derivatives $(\partial p/\partial T)_v$ and $(\partial p/\partial T)_s$, from (2.71) it follows that

$$\left(\frac{\partial p}{\partial T}\right)_v=\left(\frac{\partial p}{\partial T}\right)_s+\left(\frac{\partial p}{\partial s}\right)_T\left(\frac{\partial s}{\partial T}\right)_v. \tag{2.72}$$

Concerning Eq. (2.71) the following question can arise: since $z$ is, indeed, a function of only two variables, $x$ and $y$, the derivative $(\partial z/\partial x)$ from (2.71) is calculated with $m$ kept constant. But what is the quantity $m$, a new variable? Not at all. The quantity $z$ depends only on two variables, $x$ and $y$, and $m$ represents one more function of the same variables $x$ and $y$. We illustrate this statement with the following examples.

Let $m=x^2+2y$. We wish to find the relation between the derivatives $(\partial z/\partial x)_y$ and $(\partial z/\partial x)_{x^2+2y}$. From (2.71) it follows that

$$\left(\frac{\partial z}{\partial x}\right)_{x^2+2y}=\left(\frac{\partial z}{\partial x}\right)_y+\left(\frac{\partial z}{\partial y}\right)_x\left(\frac{\partial y}{\partial x}\right)_{x^2+2y}. \tag{2.73}$$

On the other hand, using (2.67) we can write

$$\left(\frac{\partial y}{\partial x}\right)_{x^2+2y}=-\frac{\left[\frac{\partial(x^2+2y)}{\partial x}\right]_y}{\left[\frac{\partial(x^2+2y)}{\partial y}\right]_x}, \tag{2.74}$$

whence we easily find that

$$\left(\frac{\partial y}{\partial x}\right)_{x^2+2y}=-x \tag{2.75}$$

and, therefore,

$$\left(\frac{\partial z}{\partial x}\right)_{x^2+2y}=\left(\frac{\partial z}{\partial x}\right)_y-x\left(\frac{\partial z}{\partial y}\right)_x. \tag{2.76}$$

Let us suppose, further, that $m = xy$. From (2.71) it follows that

$$\left(\frac{\partial z}{\partial x}\right)_{xy} = \left(\frac{\partial z}{\partial x}\right)_y + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_{xy}. \tag{2.77}$$

Equation (2.67) implies that

$$\left(\frac{\partial y}{\partial x}\right)_{xy} = -\frac{\left(\frac{\partial xy}{\partial x}\right)_y}{\left(\frac{\partial xy}{\partial y}\right)_x}, \tag{2.78}$$

we also note that

$$\left(\frac{\partial y}{\partial x}\right)_{xy} = -\frac{y}{x} \tag{2.79}$$

and, hence,

$$\left(\frac{\partial z}{\partial x}\right)_{xy} = \left(\frac{\partial z}{\partial x}\right)_y - \frac{y}{x}\left(\frac{\partial z}{\partial y}\right)_x. \tag{2.80}$$

As we will subsequently show, Eq. (2.71) is widely used in the various transformations of thermodynamic differential equations.

2.3.3. In Sec. 2.1.1 we pointed out that in thermodynamics the quantities $x$ and $y$ in (2.24) may be rigidly related and, hence, $z$ is in fact a function of only one variable $x$. From (2.71) it follows that

$$\frac{dz}{dx} = \left(\frac{\partial z}{\partial x}\right)_y + \left(\frac{\partial z}{\partial y}\right)_x \frac{dy}{dx}. \tag{2.81}$$

We note that $dz/dx$ is known as the *total derivative*.

In accordance with (2.8) we can write

$$\frac{dy}{dx} = \frac{dy}{dz}\,\frac{dz}{dx}. \tag{2.82}$$

From (2.81) we then obtain the following:

$$\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{dz}{dx}\right)^{-1} + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{dz}{dy}\right)^{-1} = 1. \tag{2.83}$$

On the basis of this we can obtain useful equations for calculating thermodynamic quantities (see Chap. 7).

## 2.4 The Legendre Transformation

2.4.1. The transformation that changes the roles of dependent and independent variables is called the *Legendre transformation.*[3]

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[3] This transformation, suggested by A. Legendre in 1789, is a particular case of the so-called *contact transformations*.

Let us consider an arbitrary function of several variables, $F_1(x, y, z, \ldots)$. Obviously, a total differential of this function can be written in the form

$$dF_1 = X\,dx + Y\,dy + Z\,dz + \ldots, \tag{2.84}$$

where

$$X = \left(\frac{\partial F_1}{\partial x}\right)_{y, z, \ldots}, \quad Y = \left(\frac{\partial F_1}{\partial y}\right)_{x, z, \ldots}, \quad Z = \left(\frac{\partial F_1}{\partial z}\right)_{x, y, \ldots}, \tag{2.85}$$

etc. Obviously, $X, Y, Z, \ldots$ are functions of variables $x, y, z, \ldots$.

Let us introduce the function

$$F_2 = F_1 - Xx. \tag{2.86}$$

It is obvious that

$$dF_2 = dF_1 - X\,dx - x\,dX; \tag{2.87}$$

whence, taking into account (2.84), we have

$$dF_2 = -x\,dX + Y\,dy + Z\,dz + \ldots. \tag{2.88}$$

Thus, this transformation yields the transition from independent variables $x, y, z, \ldots$ to independent variables $X, y, z, \ldots$ and, hence, $x$ becomes dependent and $X$ independent. In other words, to change the roles of dependent and independent variables, it is necessary to make use of the following relation:

$$X\,dx = d\,(Xx) - x\,dX. \tag{2.89}$$

2.4.2. As we will show below (Chap. 3), by applying the Legendre transformation (2.89) to the function $U$ we can obtain a number of important thermodynamic functions (the so-called characteristic functions); here we use the relations of type (2.89), in which variables $T$, $p$, and $\xi$ are substituted for $s$, $v$, and $w$, respectively. F. Massieu was the first to apply the Legendre transformations of thermodynamic functions in 1869.

## 2.5 The Discontinuities of Thermodynamic Functions

2.5.1. The notion of continuity of a function is one of the most important in mathematics. We recall that a function $f(x)$ is said to be continuous at a point $a$ if (a) this function is defined throughout a neighbourhood of $a$, (b) there exist limits of this function $\lim\limits_{x \to a} f(x)$ from the left and right of point $a$, and (c) these limits coincide with the value which the function assumes at $x = a$. This definition can be written thus:

$$f(a + 0) = f(a - 0) = f(a), \tag{2.90}$$

where we have introduced the following notations:

$$\lim_{x\to a+0} f(x)=f(a+0) \qquad (2.91)$$

and

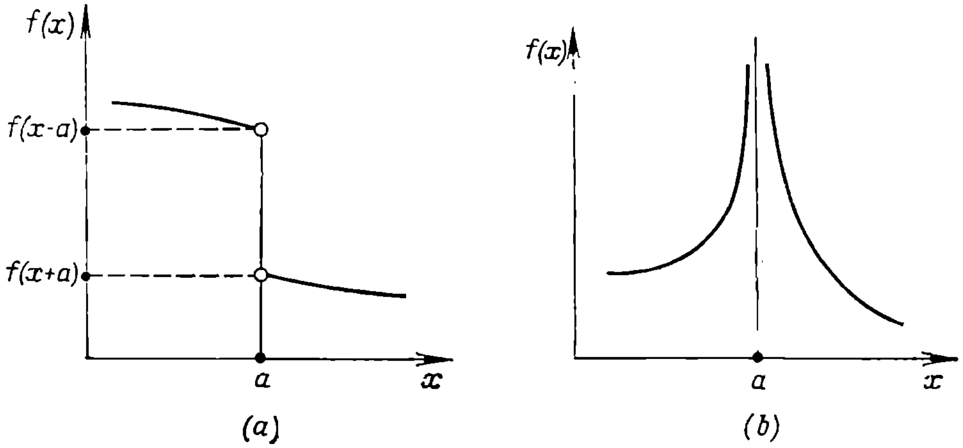
$$\lim_{x\to a-0} f(x)=f(a-0); \qquad (2.92)$$

here $x \to a+0$ means that $x$ tends to $a$ from values of $x$ greater than $a$, and $x \to a-0$ means that $x$ tends to $a$ from values of $x$ less than $a$.

If condition (2.90) is not met, then the function $f(x)$ has a discontinuity at point $a$.

It is customary to divide the points of discontinuity into two categories:

(1) Point $a$ is called a point of discontinuity of the first kind if there exist the limits of the function $f(x)$ from the left and right of $a$ but at least one of these limits, $f(a+0)$ or $f(a-0)$, is distinct from $f(a)$.



(a) (b)

Fig. 2.1

(2) All other points of discontinuity are called points of discontinuity of the second kind. Obviously, at a point of discontinuity of the second kind a function has no limit.

Examples of the points of discontinuity of a function are given in Fig. 2.1; (*a*) a discontinuity of the first kind, and (*b*) a discontinuity of the second kind.

2.5.2. In the same way as we dealt above with a function of one variable, we can introduce the notion of a continuous function of two or more variables and, correspondingly, a classification of points of discontinuity of the function. Clearly, the points of discontinuity of a function $z=z(x, y)$ can form a line of discontinuity, and the function undergoes a discontinuity when passing across this line.

It is the lines of discontinuity of a function that we have to deal with mostly in thermodynamics.

2.5.3. Thermodynamic functions are continuous throughout a thermodynamic state surface except in the regions of phase transitions. When we cross a boundary curve separating a one-phase region from a two-phase region, thermodynamic functions undergo a jump; in other words, boundary curves are the lines of discontinuity of thermodynamic functions. For some functions this is a discontinuity of the first kind. Examples are the isochoric heat capacity $c_v$, the adiabatic exponent, the sound velocity, and the Joule-Thomson coefficient. These undergo a finite jump when crossing the boundary curve. For other thermodynamic functions, such as the isobaric heat capacity $c_p$ and the quantities $(\partial v/\partial T)_p$ and $(\partial v/\partial p)_T$, this is a discontinuity of the second kind; everywhere on the boundary curve except at the critical point the functions have a limit when approaching the boundary curve from the one-phase region and become infinite when approaching the curve from the two-phase region, while at the critical point there are no limits of these functions from either left or right.

The behaviour of thermodynamic systems on the lines of discontinuity is treated in detail below, in Chaps. 6 through 8. It is convenient to consider the variation of a thermodynamic function of two variables, $z = z(x, y)$, with the value of one variable kept constant (e.g. with $y = \text{const}$), i.e. to analyze the variation of the thermodynamic function along the line $y = \text{const}$ when this line intersects the line of discontinuity of the function (boundary curve).

## 2.6 Jacobians

2.6.1. A useful tool for the operations on thermodynamic differential equations is the functional determinants, or Jacobians.

The Jacobian of $x$ and $y$ for two independent variables $m$ and $n$ is the determinant

$$\begin{vmatrix} \left(\frac{\partial x}{\partial m}\right)_n & \left(\frac{\partial x}{\partial n}\right)_m \\ \left(\frac{\partial y}{\partial m}\right)_n & \left(\frac{\partial y}{\partial n}\right)_m \end{vmatrix},$$

where $x = f_1(m, n)$ and $y = f_2(m, n)$. The customary notation is

$$\frac{\partial(x, y)}{\partial(m, n)} = \begin{vmatrix} \left(\frac{\partial x}{\partial m}\right)_n & \left(\frac{\partial x}{\partial n}\right)_m \\ \left(\frac{\partial y}{\partial m}\right)_n & \left(\frac{\partial y}{\partial n}\right)_m \end{vmatrix}. \tag{2.93}$$

It is obvious that

$$\frac{\partial(x, y)}{\partial(m, n)}=\left(\frac{\partial x}{\partial m}\right)_n\left(\frac{\partial y}{\partial n}\right)_m-\left(\frac{\partial x}{\partial n}\right)_m\left(\frac{\partial y}{\partial m}\right)_n. \qquad (2.94)$$

2.6.2. Jacobians have the following basic properties.

(1) Since according to (2.93)

$$\frac{\partial(y, x)}{\partial(m, n)}=\begin{vmatrix}\left(\frac{\partial y}{\partial m}\right)_n & \left(\frac{\partial y}{\partial n}\right)_m\\ \left(\frac{\partial x}{\partial m}\right)_n & \left(\frac{\partial x}{\partial n}\right)_m\end{vmatrix} \qquad (2.95)$$

and, therefore,

$$\frac{\partial(y, x)}{\partial(m, n)}=\left(\frac{\partial y}{\partial m}\right)_n\left(\frac{\partial x}{\partial n}\right)_m-\left(\frac{\partial y}{\partial n}\right)_m\left(\frac{\partial x}{\partial m}\right)_n, \qquad (2.96)$$

comparing (2.95) and (2.96), we see that

$$\frac{\partial(y, x)}{\partial(m, n)}=-\frac{\partial(x, y)}{\partial(m, n)}. \qquad (2.97)$$

(2) Since according to (2.93)

$$\frac{\partial(y, z)}{\partial(x, z)}=\begin{vmatrix}\left(\frac{\partial y}{\partial x}\right)_z & \left(\frac{\partial y}{\partial z}\right)_x\\ \left(\frac{\partial z}{\partial y}\right)_z & \left(\frac{\partial z}{\partial z}\right)_x\end{vmatrix}, \qquad (2.98)$$

or

$$\frac{\partial(y, z)}{\partial(x, z)}=\begin{vmatrix}\left(\frac{\partial y}{\partial x}\right)_z & \left(\frac{\partial y}{\partial z}\right)_x\\ 0 & 1\end{vmatrix}, \qquad (2.99)$$

we see that

$$\frac{\partial(y, z)}{\partial(x, z)}=\left(\frac{\partial y}{\partial x}\right)_z. \qquad (2.100)$$

It is obvious then that all partial derivatives can be represented by Jacobians.

(3) It is easy to see that

$$\frac{\partial(y, x)}{\partial(a, b)}\,\frac{\partial(a, b)}{\partial(m, n)}=\frac{\partial(y, x)}{\partial(m, n)}. \qquad (2.101)$$

(4) From (2.93) it also follows that

$$\frac{\partial(m, n)}{\partial(m, n)}=1, \qquad (2.102)$$

$$\frac{\partial(x, x)}{\partial(m, n)}=0, \qquad (2.103)$$

and

$$\frac{\partial(k, x)}{\partial(m, n)}=0 \text{ if } k=\text{const}. \qquad (2.104)$$

2.6.3. Equations (2.97), (2.100), and (2.101) make it possible to transform the partial derivatives of thermodynamic quantities quite easily.[4]

Let us transform, for instance, the quantity $(\partial T/\partial p)_s$. In accordance with (2.100) we may write

$$\left(\frac{\partial T}{\partial p}\right)_s=\frac{\partial (T, s)}{\partial (p, s)}. \tag{2.105}$$

According to (2.97),

$$\frac{\partial (T, s)}{\partial (p, s)}=-\frac{\partial (s, T)}{\partial (p, s)}, \tag{2.106}$$

while

$$\frac{\partial (s, T)}{\partial (p, s)}=\frac{\partial (s, T)}{\partial (p, T)}\Big/\frac{\partial (p, s)}{\partial (p, T)} \tag{2.107}$$

in conformity with (2.101). But according to (2.100),

$$\frac{\partial (s, T)}{\partial (p, T)}=\left(\frac{\partial s}{\partial p}\right)_T \tag{2.108}$$

and

$$\frac{\partial (p, s)}{\partial (p, T)}=\left(\frac{\partial s}{\partial T}\right)_p. \tag{2.109}$$

Consequently, we see that

$$\left(\frac{\partial T}{\partial p}\right)_s=-\left(\frac{\partial s}{\partial p}\right)_T\Big/\left(\frac{\partial s}{\partial T}\right)_p. \tag{2.110}$$

Let us now express the quantity $(\partial s/\partial T)_v$ in terms of $(\partial s/\partial T)_p$. To this end we make the following transformations:

$$\left(\frac{\partial s}{\partial T}\right)_v=\frac{\partial (s, v)}{\partial (T, v)} \tag{2.111}$$

and, in accordance with (2.101),

$$\frac{\partial (s, v)}{\partial (T, v)}=\frac{\partial (s, v)}{\partial (T, p)}\Big/\frac{\partial (s, v)}{\partial (T, p)}. \tag{2.112}$$

Since by (2.94)

$$\frac{\partial (s, v)}{\partial (T, p)}=\left(\frac{\partial s}{\partial T}\right)_p\left(\frac{\partial v}{\partial p}\right)_T-\left(\frac{\partial s}{\partial p}\right)_T\left(\frac{\partial v}{\partial T}\right)_p \tag{2.113}$$

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[4] In 1934 A.N. Shaw was the first to suggest using Jacobians for transforming thermodynamic quantities.

and

$$\frac{\partial(T, v)}{\partial(T, p)} = \left(\frac{\partial v}{\partial p}\right)_T, \qquad (2.114)$$

combining (2.111) with (2.112) and (2.68), we find that

$$\left(\frac{\partial s}{\partial T}\right)_v = \left(\frac{\partial s}{\partial T}\right)_p + \left(\frac{\partial s}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_v. \qquad (2.115)$$

2.6.4. In conclusion we note that transformations of thermodynamic quantities can be performed without resorting to Jacobians. For one, relation (2.110) obtained in the above examples readily follows from (2.67) and relation (2.115) from (2.71).

# 3 Characteristic Functions and Their Properties

## 3.1 The Basic Characteristic Functions

3.1.1. To examine the criteria for equilibrium in thermodynamic systems we first introduce a number of important thermodynamic functions.

In Chap. 1 we noted that the combined equation of the first and second laws of thermodynamics is generally written in the form (1.25):

$$T\,dS \geqslant dU + p\,dV + \xi\,dW.$$

This relationship provides an important criterion for establishing whether an isolated thermodynamic system is in equilibrium. We recall that in thermodynamics a system is called isolated if it does not exchange heat or work with the surroundings. Hence, in such a system the internal energy $U$, volume $V$, and generalized coordinate $W$ (the latter corresponds to work other than expansion work) are constant.

In accordance with the second law of thermodynamics the entropy of an isolated system tends to be maximal; in equilibrium it has the greatest possible value for such a system. Indeed, since for an isolated system $dU = 0$, $dV = 0$, and $dW = 0$, from (1.25) we see that

$$dS \geqslant 0. \tag{3.1}$$

This condition determines the evolution of an isolated system. The inequality sign corresponds to a nonequilibrium state of the system, when the system is still on its way, so to say, to equilibrium state, and the equality corresponds to a system already in equilibrium. Thus for an isolated system in an equilibrium state

$$dS = 0, \tag{3.1a}$$

which is the criterion for equilibrium of an isolated system.

But if the system is not isolated from the surrounding medium and can interact with it in some way (coupled with the medium, as is sometimes said), the criteria for equilibrium will differ from (3.2). They depend on the conditions in which the system interacts (couples) with the surroundings.

3.1.2. For a system performing only work of expansion (simple system) the following four types of interaction between the system and the surrounding medium are the most interesting: $V = \text{const}$ and $S = \text{const}$, $p = \text{const}$ and $S = \text{const}$, $V = \text{const}$ and $T = \text{const}$, and $p = \text{const}$ and $T = \text{const}$. The equilibrium criteria for each interaction are as follows.

(1) Interaction conditions $V = \text{const}$ and $S = \text{const}$. We write the combined equation for the first and second laws of thermodynamics for simple systems (1.22),

$$T\,dS \geqslant dU + p\,dV,$$

in the form

$$dU \leqslant T\,dS - p\,dV. \tag{3.2}$$

This implies that the evolution of this system, in which $dV = 0$ and $dS = 0$, is restricted by the condition

$$dU \leqslant 0. \tag{3.3}$$

Hence, in equilibrium

$$dU = 0. \tag{3.3a}$$

Thus, as the system approaches equilibrium, its internal energy decreases, becoming minimal in the equilibrium state.

(2) Interaction conditions $p = \text{const}$ and $S = \text{const}$. If, in accordance with (2.89), we apply the Legendre transformation to $p\,dV$,

$$p\,dV = d(pV) - V\,dp, \tag{3.4}$$

and use the definition of enthalpy for simple systems (1.14),

$$H = U + pV,$$

we can transform (1.22) to

$$dH \leqslant T\,dS + V\,dp. \tag{3.5}$$

This implies that a process in this system, in which $dp = 0$ and $dS = 0$, takes place in such a way that the condition

$$dH \leqslant 0 \tag{3.6}$$

is met; hence, in equilibrium

$$dH = 0. \tag{3.6a}$$

Thus, as the system approaches equilibrium, its enthalpy decreases, becoming minimal in the equilibrium state.

(3) Interaction conditions $V = \text{const}$ and $T = \text{const}$. If we apply the Legendre transformation to $T\,dS$,

$$T\,dS = d(TS) - S\,dT, \tag{3.7}$$

we can transform (1.22)

$$d(U - TS) \leqslant -S\,dT - p\,dV. \tag{3.8}$$

Introducing the notation

$$F = U - TS, \tag{3.9}$$

we write (3.8) in the form

$$dF \leqslant -S\,dT - p\,dV. \tag{3.10}$$

The thermodynamic function $F$ is called the *isochoric-isothermal potential.*

From (3.10) we can see that the evolution of this system, in which $dT = 0$ and $dV = 0$, is restricted by the condition

$$dF \leqslant 0. \tag{3.11}$$

Hence, in equilibrium

$$dF = 0. \tag{3.11a}$$

Thus, as the system approaches equilibrium, its isochoric-isothermal potential decreases, becoming minimal in the equilibrium state.

(4) Interaction conditions $p$ = const and $T$ = const. Taking into account (3.4) and (3.7), we can write Eq. (1.22) in the following form:

$$d\,(U + pV - TS) \leqslant -S\,dT + V\,dp. \tag{3.12}$$

Introducing the notation

$$\Phi = U + pV - TS, \tag{3.13}$$

we can write (3.12) in the form

$$d\Phi \leqslant -S\,dT + V\,dp. \tag{3.14}$$

The thermodynamic function $\Phi$ is called the *isobaric-isothermal potential.*

From (3.13), (1.14), and (3.9) we see that

$$\Phi = H - TS \tag{3.15}$$

and

$$\Phi = F + pV. \tag{3.16}$$

It is evident from (3.14) that a process in an isobaric-isothermal system takes place in such a way that the condition

$$d\Phi \leqslant 0 \tag{3.17}$$

is met; hence, in equilibrium

$$d\Phi = 0. \tag{3.17a}$$

Thus, as the system approaches equilibrium its isobaric-isothermal potential decreases, becoming minimal in the equilibrium state.

We have thus stated the equilibrium criteria for simple thermodynamic systems.

3.1.3. When a system performs work other than work of expansion (a complex system), the above criteria will be somewhat different. For a complex system the combined equation for the first and second laws of thermodynamics written in the form (1.24),

$$T\,dS \geqslant dU + p\,dV + dL^*,$$

where in accordance with (1.7)

$$dL^* = \xi\,dW,$$

yields the following results for the above four cases of a system interacting with the surrounding medium:

(1) Interaction conditions $V = \text{const}$ and $S = \text{const}$:

$$dU + dL^* \leqslant 0, \tag{3.18}$$

i.e. in the equilibrium state

$$dU = -dL^*; \tag{3.18a}$$

(2) Interaction conditions $p = \text{const}$ and $S = \text{const}$:

$$dH + dL^* \leqslant 0, \tag{3.19}$$

i.e. in the equilibrium state

$$dH = -dL^*; \tag{3.19a}$$

(3) Interaction conditions $V = \text{const}$ and $T = \text{const}$:

$$dF + dL^* \leqslant 0, \tag{3.20}$$

i.e. in the equilibrium state

$$dF = -dL^*; \tag{3.20a}$$

(4) Interaction conditions $p = \text{const}$ and $T = \text{const}$:

$$d\Phi + dL^* \leqslant 0, \tag{3.21}$$

i.e. in the equilibrium state

$$d\Phi = -dL^*. \tag{3.21a}$$

As for a system that interacts with the surroundings under the conditions that $U$ and $V$ are constant, it is clear that when the system is complex, these conditions do not yet ensure that it is isolated (for this it would also be necessary to have $W$ constant). We see that in this case, as is evident from Eq. (1.24),

$$T\,dS \geqslant dL^*, \tag{3.22}$$

or, which is the same,

$$dS \geqslant \frac{\xi}{T}\,dW, \tag{3.23}$$

i.e. in the equilibrium state

$$dS = \frac{\xi}{T}\, dW. \tag{3.24}$$

The quantities $U$, $H$, $F$, and $\Phi$ are known as *characteristic functions*. It is important to note that the functions $F$ and $\Phi$ are formed from state functions $S$, $U$, and $H$ and, hence, are state functions, too. Therefore, all four characteristic functions are state functions and, hence, their differentials are total.

We can see from Eqs. (3.18a), (3.19a), (3.20a), and (3.21a) that the work a complex system can perform under given conditions of coupling with the surrounding medium (after we have subtracted the work of expansion[1]) is equal to the decrease in the corresponding characteristic function. This is why, by a well-known analogy with mechanics, the characteristic functions $U$, $H$, $F$, and $\Phi$ are called *thermodynamic potentials*.

3.1.4. Characteristic functions have the following important property: if a characteristic function is known in terms of the corresponding variables (different for each characteristic function), it can be used to calculate any thermodynamic quantity. This is easily verified.

(1) From Eq. (1.22) written in the form

$$dU = T\, dS - p\, dV \tag{3.25}$$

and combined with Eq. (2.63), we see that

$$\left(\frac{\partial U}{\partial S}\right)_V = T \tag{3.26}$$

and

$$\left(\frac{\partial U}{\partial V}\right)_S = -p. \tag{3.27}$$

Thus, if the function $U$ is expressed in terms of the variables $V$ and $S$, differentiating $U$ with respect to one of these variables, provided that the other variable is kept constant, enables us to determine the values of $p$ and $T$. As a result the values of $U$, $V$, $S$, $p$, and $T$ are known, and we can easily calculate $H$, $F$, and $\Phi$.

(2) Taking (3.4) and (1.14) into account, we can write Eq. (3.25) in the form

$$dH = T\, dS + V\, dp; \tag{3.28}$$

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[1] In accordance with (1.6),

$$dL^* = dL - p\, dV,$$

which is why $L^*$ is sometimes called the *net work*.

whence it follows that[2]

$$\left(\frac{\partial H}{\partial S}\right)_p = T \tag{3.29}$$

and

$$\left(\frac{\partial H}{\partial p}\right)_S = V. \tag{3.30}$$

Thus, if the function $H$ is expressed in terms of the variables $p$ and $S$, differentiating $H$ with respect to one of these variables, provided that the other variable is kept constant, we can determine $T$ and $V$. Whence we know the values of $H$, $V$, $S$, $p$, and $T$ and can easily calculate $U$, $F$, and $\Phi$.

(3) If we use (3.7) to replace $T\,dS$ in Eq. (3.25) and take into account (3.9), we find that

$$dF = -S\,dT - p\,dV. \tag{3.31}$$

It is evident from this relation that

$$\left(\frac{\partial F}{\partial T}\right)_V = -S \tag{3.32}$$

and

$$\left(\frac{\partial F}{\partial V}\right)_T = -p. \tag{3.33}$$

Thus, if the function $F$ is expressed in terms of the variables $V$ and $T$, differentiating $F$ with respect to one of these variables, provided that the other variable is kept constant, we can determine $S$ and $p$. Whence we know the values of $F$, $S$, $p$, $V$, and $T$ and can calculate $U$, $H$, and $\Phi$.

(4) Finally, using (3.9) and (3.15), we find from (3.28) that

$$d\Phi = -S\,dT + V\,dp. \tag{3.34}$$

Whence it is clear that

$$\left(\frac{\partial \Phi}{\partial T}\right)_p = -S \tag{3.35}$$

and

$$\left(\frac{\partial \Phi}{\partial p}\right)_T = V. \tag{3.36}$$

Thus, if the function $\Phi$ is expressed in terms of the variables $p$ and $T$, then differentiating $\Phi$ with respect to one of these variables, provided that the other variable is kept constant, we can determine $S$

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[2] The reader must bear in mind that any function formed by a simple algebraic combination of state functions is itself a state function and, therefore, its differential is total.

and $V$. Whence we know the values of $\Phi$, $S$, $p$, $V$, and $T$ and can calculate $U$, $H$, and $F$.

3.1.5. Characteristic functions are additive quantities. Consequently, the values of characteristic functions for an entire thermodynamic system can be represented as a product of a specific (per unit mass) characteristic function by the mass of substance in the system:

Internal energy

$$U = uG. \tag{3.37}$$

Enthalpy

$$H = hG, \tag{3.38}$$

where

$$h = u + pv. \tag{3.39}$$

Isochoric-isothermal potential

$$F = fG, \tag{3.40}$$

where

$$f = u - Ts. \tag{3.41}$$

Isobaric-isothermal potential

$$\Phi = \varphi G, \tag{3.42}$$

where

$$\varphi = u + pv - Ts, \tag{3.43}$$

or, which is the same,

$$\varphi = h - Ts \tag{3.44}$$

and

$$\varphi = f + pv. \tag{3.45}$$

It is clear of course that if the amount of substance in the system is fixed ($G$ = const), the relations (3.25)-(3.27) can be represented in the following form:

$$du = T\,ds - p\,dv, \tag{3.25a}$$

$$\left(\frac{\partial u}{\partial s}\right)_v = T, \tag{3.26a}$$

$$\left(\frac{\partial u}{\partial v}\right)_s = -p; \tag{3.27a}$$

the relations (3.28)-(3.30) in the form

$$dh = T\,ds + v\,dp, \tag{3.28a}$$

$$\left(\frac{\partial h}{\partial s}\right)_p = T, \tag{3.29a}$$

$$\left(\frac{\partial h}{\partial p}\right)_s = v; \tag{3.30a}$$

the relations (3.31)-(3.33) in the form

$$df = -s\,dT - p\,dv, \tag{3.31a}$$

$$\left(\frac{\partial f}{\partial T}\right)_v = -s, \tag{3.32a}$$

$$\left(\frac{\partial f}{\partial v}\right)_T = -p; \tag{3.33a}$$

and the relations (3.34)-(3.36) in the form

$$d\varphi = -s\,dT + v\,dp, \tag{3.34a}$$

$$\left(\frac{\partial \varphi}{\partial T}\right)_p = -s, \tag{3.35a}$$

$$\left(\frac{\partial \varphi}{\partial p}\right)_T = v. \tag{3.36a}$$

3.1.6. Let us now consider the equilibrium criteria for systems in other conditions of interaction with the surroundings; namely, when in addition to the conditions enumerated above the values of generalized force $\xi$ or generalized coordinate $W$, which characterize the given type of work, remain constant.

As for an isolated system ($U$, $V$, and $W$ constant), according to the second law of thermodynamics the equilibrium criterion, as noted above, states that the system's entropy must be maximal; this is evident, in particular, from the combined equation of the first and second laws of thermodynamics for a complex system written in the form (1.25):

$$T\,dS \geqslant dU + p\,dV + \xi\,dW.$$

If we turn to systems that interact with the surrounding medium, we discover that the following types of interaction are of interest: $V$, $S$, and $W$ are constant; $p$, $S$, and $\xi$ are constant; $V$, $T$, and $W$ are constant; and $p$, $T$, and $\xi$ are constant.

To find the equilibrium criteria for such systems we will use the method employed above.

(1) Interaction conditions $V$, $S$, and $W$ constant. If we write Eq. (1.25) in the form

$$dU \leqslant T\,dS - p\,dV - \xi\,dW, \tag{3.46}$$

we can see that the evolution of a system, in which $dV = 0$, $dS = 0$, and $dW = 0$, is determined by the condition

$$dU \leqslant 0; \tag{3.47}$$

hence in equilibrium

$$dU = 0. \tag{3.47a}$$

Thus the criterion for equilibrium for a complex system, in which $V$, $S$, and $W$ are constant, is the same as for a simple system with $V$ and $S$ constant (see Eqs. (3.3) and (3.3a)).

(2) Interaction conditions $p$, $S$, and $\xi$ constant. The product $\xi\, dW$ in Eq. (1.25) can be represented via the Legendre transformation (2.89) as

$$\xi\, dW = d(\xi W) - W\, d\xi \tag{3.48}$$

Combining this relation with (1.14) and (3.4), we can transform Eq. (1.25) to

$$d(H + \xi W) \leqslant T\, dS + V\, dp + W\, d\xi. \tag{3.49}$$

From (1.14) and (1.15) it is evident that

$$H + \xi W = H^*; \tag{3.50}$$

using this relation, we can write (3.49) as

$$dH^* \leqslant T\, dS + V\, dp + W\, d\xi. \tag{3.51}$$

We can see that in a complex system in which $dp = 0$, $dS = 0$, and $d\xi = 0$ the evolution is determined by the condition

$$dH^* \leqslant 0; \tag{3.52}$$

hence in the equilibrium state

$$dH^* = 0. \tag{3.52a}$$

The reader will recall that the quantity $H^*$ is the enthalpy of a complex system; it is related to the enthalpy $H$ by Eq. (3.50), and in accordance with (1.15)

$$H^* = U + pV + \xi W.$$

Thus, the equilibrium criterion for the complex system under consideration is the same as for the simple system in which $p$ and $S$ are constant (see Eqs. (3.6) and (3.6a)), the difference being that the quantity $H^*$ in Eqs. (3.52) and (3.52a) differs from the usual enthalpy $H$.

(3) Interaction conditions $V$, $T$, and $W$ constant. If we use Eqs. (3.7) and (3.9), we can write (1.25) as

$$dF \leqslant -S\, dT - p\, dV - \xi\, dW. \tag{3.53}$$

It follows that in a complex system in which $dV = 0$, $dT = 0$, and $dW = 0$ the evolution is determined by the condition

$$dF \leqslant 0, \tag{3.54}$$

i.e. in equilibrium

$$dF = 0. \tag{3.54a}$$

Thus, the equilibrium criterion for this complex system is the same as for a simple isochoric-isothermal system (see Eqs. (3.11) and (3.11a)).

(4) Interaction conditions $p$, $T$, and $\xi$ constant. Considering (3.4), (3.7), (3.13), and (3.48), we can transform Eq. (1.25) to

$$d(\Phi + \xi W) \leqslant -S\,dT + V\,dp + W\,d\xi. \tag{3.55}$$

We introduce the notation

$$\Phi^* = \Phi + \xi W. \tag{3.56}$$

Then (3.55) becomes

$$d\Phi^* \leqslant -S\,dT + V\,dp + W\,d\xi. \tag{3.57}$$

Whence it follows that in a system in which $dp = 0$, $dT = 0$, and $d\xi = 0$ all processes occur in such a way that

$$d\Phi^* \leqslant 0, \tag{3.58}$$

i.e. in equilibrium

$$d\Phi^* = 0. \tag{3.58a}$$

The quantity $\Phi^*$ can be regarded as the isobaric-isothermal potential for a complex system. This quantity is related to the common isobaric-isothermal potential via Eq. (3.56).

From (3.13), (3.15), (3.16), (3.50), and (3.56) we see that

$$\Phi^* = U + pV + \xi W - TS, \tag{3.59}$$

$$\Phi^* = H^* - TS, \tag{3.60}$$

and

$$\Phi^* = F + pV + \xi W. \tag{3.61}$$

In this form the equilibrium criterion for a complex system is similar to that for a simple system (see Eqs. (3.17) and (3.17a)), the difference being that Eqs. (3.58) and (3.58a) contain $\Phi^*$ instead of the usual isobaric-isothermal potential $\Phi$.

These are the criteria of equilibrium for thermodynamic systems that perform other work besides work of expansion and whose conditions of interaction with the surroundings are such that, in addition to the usual interaction conditions, either $\xi$ or $W$ is kept constant.

3.1.7. In conclusion let us consider relationships similar to Eqs. (3.25) through (3.45) for the case of a complex thermodynamic system.

(1) From Eq. (1.30) written in the form

$$dU = T\,dS - p\,dv - \xi\,dW, \tag{3.62}$$

we have

$$\left(\frac{\partial U}{\partial S}\right)_{V,\,W} = T, \tag{3.63}$$

$$\left(\frac{\partial U}{\partial V}\right)_{S,\,W} = -p, \tag{3.64}$$

and

$$\left(\frac{\partial U}{\partial W}\right)_{S,\,V} = -\xi. \tag{3.65}$$

If the amount of substance in the system remains unchanged ($G$ = const), we can write the same relations for specific quantities:

$$du = T\,ds - p\,dv - \xi\,dw, \tag{3.62a}$$

$$\left(\frac{\partial u}{\partial s}\right)_{v,\,w} = T, \tag{3.63a}$$

$$\left(\frac{\partial u}{\partial v}\right)_{s,\,w} = -p, \tag{3.64a}$$

and

$$\left(\frac{\partial u}{\partial w}\right)_{s,\,v} = -\xi. \tag{3.65a}$$

(2) Combining (3.4), (3.48), and (3.50), we can transform Eq. (3.62) to

$$dH^* = T\,dS + V\,dp + W\,d\xi. \tag{3.66}$$

Whence it is evident that

$$\left(\frac{\partial H^*}{\partial S}\right)_{p,\,\xi} = T, \tag{3.67}$$

$$\left(\frac{\partial H^*}{\partial p}\right)_{S,\,\xi} = V, \tag{3.68}$$

$$\left(\frac{\partial H^*}{\partial \xi}\right)_{S,\,p} = W. \tag{3.69}$$

For the specific quantities the relations are as follows:

$$dh^* = T\,ds + v\,dp + w\,d\xi, \tag{3.66a}$$

$$\left(\frac{\partial h^*}{\partial s}\right)_{p,\,\xi} = T, \tag{3.67a}$$

$$\left(\frac{\partial h^*}{\partial p}\right)_{s,\,\xi} = v, \tag{3.68a}$$

and

$$\left(\frac{\partial h^*}{\partial \xi}\right)_{s,\,p} = w. \tag{3.69a}$$

Here, obviously,

$$h^* = h + \xi w, \tag{3.50a}$$

or

$$h^* = u + pv + \xi w \tag{3.53a}$$

and

$$H^* = h^* G. \tag{3.38a}$$

(3) If we substitute the quantity $T\,dS$ in Eq. (3.62) by applying (3.7) and bear in mind (3.9), we find that

$$dF = -S\,dT - p\,dV - \xi\,dW, \tag{3.70}$$

which implies that

$$\left(\frac{\partial F}{\partial T}\right)_{V,\,W} = -S, \tag{3.71}$$

$$\left(\frac{\partial F}{\partial V}\right)_{T,\,W} = -p, \tag{3.72}$$

and

$$\left(\frac{\partial F}{\partial W}\right)_{T,\,V} = -\xi. \tag{3.73}$$

The relations for specific quantities are written in similar form:

$$df = -s\,dT - p\,dv - \xi\,dw, \tag{3.70a}$$

$$\left(\frac{\partial f}{\partial T}\right)_{v,\,w} = -s, \tag{3.71a}$$

$$\left(\frac{\partial f}{\partial v}\right)_{T,\,w} = -p, \tag{3.72a}$$

and

$$\left(\frac{\partial f}{\partial w}\right)_{T,\,v} = -\xi. \tag{3.73a}$$

(4) Finally, substituting in (3.66) the quantity $T\,dS$ with the help of (3.7) and bearing in mind (3.60), we get

$$d\Phi^* = -S\,dT + V\,dp + W\,d\xi, \tag{3.74}$$

whence

$$\left(\frac{\partial \Phi^*}{\partial T}\right)_{p,\,\xi} = -S, \tag{3.75}$$

$$\left(\frac{\partial \Phi^*}{\partial p}\right)_{T,\,\xi} = V, \tag{3.76}$$

and

$$\left(\frac{\partial \Phi^*}{\partial \xi}\right)_{T,\,p} = W. \tag{3.77}$$

Similar relations for specific quantities have the following form:

$$d\varphi^* = -s\,dT + v\,dp + w\,d\xi, \tag{3.74a}$$

$$\left(\frac{\partial\varphi^*}{\partial T}\right)_{p,\,\xi} = -s, \tag{3.75a}$$

$$\left(\frac{\partial\varphi^*}{\partial p}\right)_{T,\,\xi} = v, \tag{3.76a}$$

and

$$\left(\frac{\partial\varphi^*}{\partial \xi}\right)_{T,\,p} = w. \tag{3.77a}$$

From (3.56) and (3.59) through (3.61) it is clear that

$$\varphi^* = \varphi + \xi w, \tag{3.56a}$$

or, which is the same,

$$\varphi^* = u + pv + \xi w - Ts, \tag{3.59a}$$

$$\varphi^* = h^* - Ts, \tag{3.60a}$$

and

$$\varphi^* = f + pv + \xi w. \tag{3.61a}$$

It is also clear that

$$\Phi^* = \varphi^* G. \tag{3.42a}$$

## 3.2 The Chemical Potential

3.2.1. The chemical potential is one of the most important thermodynamic functions.

The chemical potential of a substance is its mass specific isobaric-isothermal potential. For simple systems it is defined by relation (3.43)

$$\varphi = u + pv - Ts,$$

while for complex systems by (3.59a)

$$\varphi^* = u + pv + \xi w - Ts.$$

The chemical potential occupies a special position with respect to other mass specific thermodynamic potentials, such as the internal energy $u$, enthalpy $h$ (or $h^*$), and isochoric-isothermal potential $f$. The explanation is as follows.

3.2.2. When we considered the equilibrium criteria for thermodynamic systems that interact with the surrounding medium, we tacitly assumed that the amount of substance $G$ in the system does not change. However, in a number of problems it is necessary to establish how the thermodynamic potentials of the system change when a certain amount of substance is taken from or added to the system.

(Naturally, the substance added must have the same state parameters as the main substance.) Hence we must find the quantities:

(a) simple systems

$\left(\frac{\partial U}{\partial G}\right)_{V, S}$ for systems with $V$ and $S$ constant, $\left(\frac{\partial H}{\partial G}\right)_{p, S}$ for systems with $p$ and $S$ constant, $\left(\frac{\partial F}{\partial G}\right)_{V, T}$ for systems with $V$ and $T$ constant, $\left(\frac{\partial \Phi}{\partial G}\right)_{p, T}$ for systems with $p$ and $T$ constant,

(b) complex systems

$\left(\frac{\partial U}{\partial G}\right)_{V, S, W}$ for systems with $V$, $S$, and $W$ constant, $\left(\frac{\partial H^*}{\partial G}\right)_{p, S, \xi}$ for systems with $p$, $S$, and $\xi$ constant, $\left(\frac{\partial F}{\partial G}\right)_{V, T, W}$ for systems with $V$, $T$, and $W$ constant, $\left(\frac{\partial \Phi^*}{\partial G}\right)_{p, T, \xi}$ for systems with $p$, $T$, and $\xi$ constant.

3.2.3. Often we encounter a rather widespread fallacy. The relations for simple systems given above, namely

$$U = uG, \tag{3.37}$$

$$H = hG, \tag{3.38}$$

$$F = fG, \tag{3.40}$$

$$\Phi = \varphi G, \tag{3.42}$$

and the equivalent relations for complex systems yield, it may appear at first glance, the trivial conclusion that $(\partial U/\partial G)_{V,S}$ is equal to $u$, $(\partial H/\partial G)_{p,S}$ to $h$, $(\partial F/\partial G)_{V,T}$ to $f$, and so on. This conclusion is wrong. Consider, for example, the derivative $(\partial U/\partial G)_{V,S}$. If the derivative $\partial U/\partial G$ were computed under the condition that the state parameters were constant (say, $s$ and $v$ were constant), the specific internal energy $u$ would also be constant and from (3.37) it would follow that

$$\left(\frac{\partial U}{\partial G}\right)_{s, v} = u. \tag{3.43}$$

However, the point is that $(\partial U/\partial G)_{S,V}$ is computed provided that the values of entropy and volume of the entire system are constant ($S$ and $V$ are constant), whereas from the elementary relations of additivity of entropy

$$S = sG \tag{3.78}$$

and volume

$$V = vG \tag{3.79}$$

it is clear that, if $S$ and $V$ are constant and $G$ varies, the values of the specific quantities $s$ and $v$ (and, naturally, all other state parameters of the system) also vary, and so does the value of $u$. It is obvious then that

$$\left(\frac{\partial U}{\partial G}\right)_{V,\,S} \neq \left(\frac{\partial U}{\partial G}\right)_{v,\,s}. \qquad (3.80)$$

The reader must clearly realize the fundamental difference between these derivatives. The following quantities differ in the same way: $(\partial H/\partial G)_{p,\,S}$ and $(\partial H/\partial G)_{p,s} \equiv h$, and $(\partial F/\partial G)_{V,\,T}$ and $(\partial F/\partial G)_{v,\,T} \equiv f$.

3.2.4. Now let us compute the derivatives of the thermodynamic quantities listed in Sec. 3.2.1.

(1) **The derivative $(\partial U/\partial G)_{V,\,S}$.** It is evident that (see (3.37))

$$\left(\frac{\partial U}{\partial G}\right)_{V,\,S} = \left(\frac{\partial uG}{\partial G}\right)_{V,\,S}, \qquad (3.81)$$

whence

$$\left(\frac{\partial U}{\partial G}\right)_{V,\,S} = u + G\left(\frac{\partial u}{\partial G}\right)_{V,\,S}. \qquad (3.82)$$

Further, in accordance with (2.71) we can write

$$\left(\frac{\partial u}{\partial G}\right)_{V,\,S} = \left(\frac{\partial u}{\partial G}\right)_{V,\,s} + \left(\frac{\partial u}{\partial s}\right)_{V,\,G}\left(\frac{\partial s}{\partial G}\right)_{V,\,S}. \qquad (3.83)$$

In a similar manner we can write for the quantity $(\partial u/\partial G)_{V,s}$ in Eq. (3.83) the following:

$$\left(\frac{\partial u}{\partial G}\right)_{V,\,s} = \left(\frac{\partial v}{\partial G}\right)_{v,\,s} + \left(\frac{\partial u}{\partial v}\right)_{G,\,s}\left(\frac{\partial v}{\partial G}\right)_{V,\,s}; \qquad (3.84)$$

hence, (3.83) can be represented in the following form:

$$\left(\frac{\partial u}{\partial G}\right)_{V,\,S} = \left(\frac{\partial u}{\partial G}\right)_{v,\,s} + \left(\frac{\partial u}{\partial v}\right)_{G,\,s}\left(\frac{\partial v}{\partial G}\right)_{V,\,s} + \left(\frac{\partial u}{\partial s}\right)_{V,\,G}\left(\frac{\partial s}{\partial G}\right)_{V,\,S}. \qquad (3.85)$$

Let us consider the partial derivatives on the right-hand side of this relation.

First, since it is obvious that if $v$ and $s$ are constant, i.e. thermodynamic parameters of the system remain unchanged, by virtue of this $u$ = const; consequently,

$$\left(\frac{\partial u}{\partial G}\right)_{v,\,s} = 0. \qquad (3.86)$$

Second, the fact that the quantity $G$ is kept constant in the process of differentiation is not necessarily applied to specific quantities; hence it is understood that $(\partial u/\partial v)_{G,s}$ is simply the derivative $(\partial u/\partial v)_s$. Therefore, taking into account (3.27a), we find that

$$\left(\frac{\partial u}{\partial v}\right)_{G,\,s} = -p. \qquad (3.87)$$

Third, since, as it is clear from (3.79),

$$v = V/G, \tag{3.79a}$$

we see that

$$\left(\frac{\partial v}{\partial G}\right)_{V,\,s} = -\frac{V}{G^2}, \tag{3.88}$$

or, which is the same,

$$\left(\frac{\partial v}{\partial G}\right)_{V,\,s} = -\frac{v}{G}. \tag{3.89}$$

Fourth, if in the process of differentiation $V$ and $G$ remain constant, then $v$ is constant and, if we bear in mind (3.26a), the derivative $(\partial u/\partial s)_{V,G}$ can be written thus:

$$\left(\frac{\partial u}{\partial s}\right)_{V,\,G} = T. \tag{3.90}$$

Last, since from (3.78) it is evident that

$$s = S/G, \tag{3.78a}$$

we see that

$$\left(\frac{\partial s}{\partial G}\right)_{V,\,S} = -\frac{S}{G^2}, \tag{3.91}$$

or, which is the same,

$$\left(\frac{\partial s}{\partial G}\right)_{V,\,S} = -\frac{s}{G}. \tag{3.92}$$

Substituting (3.86), (3.87), (3.89), (3.90), and (3.92) into (3.85), we obtain

$$\left(\frac{\partial u}{\partial G}\right)_{V,\,S} = \frac{pv - Ts}{G}. \tag{3.93}$$

Combining this with (3.82), we find that

$$\left(\frac{\partial U}{\partial G}\right)_{V,\,S} = u + pv - Ts, \tag{3.94}$$

or, bearing in mind (3.43),

$$\left(\frac{\partial U}{\partial G}\right)_{V,\,S} = \varphi. \tag{3.95}$$

(2) **The derivative $(\partial H/\partial G)_{p,\,S}$.** From (3.38) it is clear that

$$\left(\frac{\partial H}{\partial G}\right)_{p,\,S} = \left(\frac{\partial hG}{\partial G}\right)_{p,\,S} \tag{3.96}$$

and, hence,

$$\left(\frac{\partial H}{\partial G}\right)_{p,\,S} = h + G\left(\frac{\partial h}{\partial G}\right)_{p,\,S}. \tag{3.97}$$

In accordance with (2.71) we write

$$\left(\frac{\partial h}{\partial G}\right)_{p,\,S}=\left(\frac{\partial h}{\partial G}\right)_{p,\,s}+\left(\frac{\partial h}{\partial s}\right)_{p,\,G}\left(\frac{\partial s}{\partial G}\right)_{p,\,S}, \tag{3.98}$$

which implies that

$$\left(\frac{\partial h}{\partial G}\right)_{p,\,s}=0. \tag{3.99}$$

In fact, if the state parameters of the system remain unchanged ($p$ and $s$ are constant), $h$ cannot vary either.

It is obvious (see (3.29a)) that

$$\left(\frac{\partial h}{\partial s}\right)_{p,\,G}=T, \tag{3.100}$$

while if we bear in mind (3.78a)

$$s=S/G,$$

we obtain

$$\left(\frac{\partial s}{\partial G}\right)_{p,\,S}=-\frac{S}{G^2}, \tag{3.101}$$

or, which is the same,

$$\left(\frac{\partial s}{\partial G}\right)_{p,\,S}=-\frac{s}{G}. \tag{3.102}$$

Substituting (3.99), (3.100), and (3.102) into (3.98), we get

$$\left(\frac{\partial h}{\partial G}\right)_{p,\,S}=-\frac{Ts}{G}. \tag{3.103}$$

Therefore, Eq. (3.97) can be written in the form

$$\left(\frac{\partial H}{\partial G}\right)_{p,\,S}=h-Ts, \tag{3.104}$$

whence it is clear (see (3.44)) that

$$\left(\frac{\partial H}{\partial G}\right)_{p,\,S}=\varphi. \tag{3.105}$$

(3) **The derivative $(\partial F/\partial G)_{V,\,T}$.** From (3.40) it is evident that

$$\left(\frac{\partial F}{\partial G}\right)_{V,\,T}=\left(\frac{\partial fG}{\partial G}\right)_{V,\,T}, \tag{3.106}$$

or, which is the same,

$$\left(\frac{\partial F}{\partial G}\right)_{V,\,T}=f+G\left(\frac{\partial f}{\partial G}\right)_{V,\,T}. \tag{3.107}$$

If we use (2.71), we find that

$$\left(\frac{\partial f}{\partial G}\right)_{V,\,T}=\left(\frac{\partial f}{\partial G}\right)_{v,\,T}+\left(\frac{\partial f}{\partial v}\right)_{G,\,T}\left(\frac{\partial v}{\partial G}\right)_{V,\,T}. \tag{3.108}$$

If $v$ and $T$ are constant, then $f$ is constant too. Hence,

$$\left(\frac{\partial f}{\partial G}\right)_{v,\,T}=0. \tag{3.109}$$

From (3.33a) it is clear that

$$\left(\frac{\partial f}{\partial v}\right)_{G,\,T}=-p, \tag{3.110}$$

while from (3.79a)

$$v=V/G$$

it is clear that

$$\left(\frac{\partial v}{\partial G}\right)_{V,\,T}=-\frac{V}{G^2}, \tag{3.111}$$

or

$$\left(\frac{\partial v}{\partial G}\right)_{V,\,T}=-\frac{v}{G}. \tag{3.112}$$

Combining (3.109), (3.110), and (3.112), we find from (3.108) that

$$\left(\frac{\partial f}{\partial G}\right)_{V,\,T}=\frac{pv}{G}. \tag{3.113}$$

If we substitute this value into (3.107), we obtain

$$\left(\frac{\partial F}{\partial G}\right)_{V,\,T}=f+pv, \tag{3.114}$$

or, using (3.45),

$$\left(\frac{\partial F}{\partial G}\right)_{V,\,T}=\varphi. \tag{3.115}$$

(4) **The derivative** $(\partial\Phi/\partial G)_{p,\,T}$. This is computed very simply. Indeed, from (3.42) it is clear that

$$\left(\frac{\partial \Phi}{\partial G}\right)_{p,\,T}=\varphi+G\left(\frac{\partial \varphi}{\partial G}\right)_{p,\,T}. \tag{3.116}$$

But since at $p$ = constant and $T$ = constant $\varphi$ is also constant, naturally

$$\left(\frac{\partial \varphi}{\partial G}\right)_{p,\,T}=0 \tag{3.117}$$

and, hence,

$$\left(\frac{\partial \Phi}{\partial G}\right)_{p,\,T}=\varphi. \tag{3.118}$$

3.2.5. Thus, we have arrived at a somewhat unexpected conclusion that for systems in which $V$ and $S$ are constant, $p$ and $S$ are constant, $V$ and $T$ are constant, or $p$ and $T$ are constant the derivative of the corresponding characteristic function with respect to the amount of substance in the system is equal to $\varphi$, i.e.

$$\left(\frac{\partial U}{\partial G}\right)_{V,\,S}=\left(\frac{\partial H}{\partial G}\right)_{p,\,S}=\left(\frac{\partial F}{\partial G}\right)_{V,\,T}=\left(\frac{\partial \Phi}{\partial G}\right)_{p,\,T}=\varphi. \tag{3.119}$$

It is easy to show that for the corresponding complex systems we have similar relationships:

$$\left(\frac{\partial U}{\partial G}\right)_{V,\,S,\,W}=\left(\frac{\partial H^*}{\partial G}\right)_{p,\,S,\,\xi}=\left(\frac{\partial F}{\partial G}\right)_{V,\,T,\,W}=\left(\frac{\partial \Phi^*}{\partial G}\right)_{p,\,T,\,\xi}=\varphi^*, \tag{3.120}$$

where $\varphi^*$ is defined in (3.59a).

Thus, the quantity $\varphi$ (or $\varphi^*$ for complex systems) has a remarkable property: it enables us to compute the variation of a characteristic function of any system when the amount of a substance in the system is varied; for this reason this quantity has been termed the *chemical potential.*

3.2.6. It is appropriate to note that the question of the chemical potential is usually presented in thermodynamics courses in such a concise form that the reader often does not understand why this seemingly ordinary thermodynamic function, the specific isobaric-isothermal potential, occupies a special place as compared to other specific characteristic functions. We may often come across gross errors in both presenting these questions and using this quantity in computations. The reason for this, in our opinion, is also the fact that when employing the traditional method of deriving relations (3.120), the mathematical and physical sense of the operations performed is concealed. Let us consider, for example, how the quantity $(\partial U/\partial G)_{V,S}$ is calculated in thermodynamics.

From (3.37)

$$U = uG$$

it follows that

$$dU = G\,du + u\,dG; \tag{3.121}$$

since in accordance with (3.25a)

$$du = T\,ds - p\,dv,$$

Eq. (3.80) can be transformed to

$$dU = TG\,ds - pG\,dv + u\,dG. \tag{3.122}$$

Using Legendre transformations

$$G\,ds = d\,(Gs) - s\,dG \tag{3.123}$$

and

$$G\,dv = d\,(Gv) = v\,dG \tag{3.124}$$

und combining (3.78) with (3.79), from (3.122) we find that

$$dU = (u + pv - Ts)\, dG + T\, dS - p\, dV. \tag{3.125}$$

Since in the system under consideration $S$ and $V$ are constant, taking into account (3.43) we obtain for the given system

$$dU = \varphi\, dG \tag{3.126}$$

and whence

$$\left(\frac{\partial U}{\partial G}\right)_{S,\,V} = \varphi.$$

The method of deriving relations (3.120) given above, Sec. 3.2.4, appears to have certain advantages as compared to the method considered here.

3.2.7. One more remark is in order. As noted earlier (see Sec. 3.1.1), the quantity that characterizes the equilibrium state of an isolated system is entropy (in the equilibrium state entropy is maximal). Entropy is not a thermodynamic potential. It is interesting to note, however, that the derivative of the entropy of an isolated system with respect to $G$ is closely related to the chemical potential. Indeed, (3.78) yields

$$\left(\frac{\partial S}{\partial G}\right)_{U,\,V} = s + G\left(\frac{\partial s}{\partial G}\right)_{U,\,V}. \tag{3.127}$$

Using (2.71), we find that

$$\left(\frac{\partial s}{\partial G}\right)_{U,\,V} = \left(\frac{\partial s}{\partial G}\right)_{u,\,V} + \left(\frac{\partial s}{\partial u}\right)_{G,\,V}\left(\frac{\partial u}{\partial G}\right)_{U,\,V} \tag{3.128}$$

and, in its turn,

$$\left(\frac{\partial s}{\partial G}\right)_{u,\,V} = \left(\frac{\partial s}{\partial G}\right)_{u,\,v} + \left(\frac{\partial s}{\partial v}\right)_{u,\,G}\left(\frac{\partial v}{\partial G}\right)_{u,\,V}. \tag{3.129}$$

These relations yield

$$\left(\frac{\partial s}{\partial G}\right)_{U,\,V} = \left(\frac{\partial s}{\partial G}\right)_{u,\,v} + \left(\frac{\partial s}{\partial v}\right)_{u,\,G}\left(\frac{\partial v}{\partial G}\right)_{u,\,V} + \left(\frac{\partial s}{\partial u}\right)_{G,\,V}\left(\frac{\partial u}{\partial G}\right)_{U,\,V}. \tag{3.130}$$

Next, since (a)

$$\left(\frac{\partial s}{\partial G}\right)_{u,\,v} = 0, \tag{3.131}$$

(b) it is obvious from (1.27a) that

$$\left(\frac{\partial s}{\partial v}\right)_{u,\,G} = \frac{p}{T}, \tag{3.132}$$

(c) according to (3.26)

$$\left(\frac{\partial s}{\partial u}\right)_{G,\,V}=\frac{1}{T}, \tag{3.133}$$

and from (3.37) and (3.79) it follows, respectively, that (d)

$$\left(\frac{\partial u}{\partial G}\right)_{U,\,V}=-\frac{u}{G} \tag{3.134}$$

and (e)

$$\left(\frac{\partial v}{\partial G}\right)_{u,\,V}=-\frac{v}{G}, \tag{3.135}$$

from (3.130) we obtain

$$\left(\frac{\partial s}{\partial G}\right)_{U,\,V}=-\frac{u+pv}{TG}. \tag{3.136}$$

If we substitute (3.136) into (3.127), we find that

$$\left(\frac{\partial S}{\partial G}\right)_{U,\,V}=-\frac{u+pv-Ts}{T}, \tag{3.137}$$

or, using (3.143),

$$\left(\frac{\partial S}{\partial G}\right)_{U,\,V}=-\frac{\varphi}{T}. \tag{3.138}$$

Obviously, this relation refers to a simple isolated system ($U$ and $V$ constant). A similar relation can be obtained for a complex isolated system ($U$, $V$, and $W$ constant):

$$\left(\frac{\partial S}{\partial G}\right)_{U,\,V,\,W}=-\frac{\varphi^*}{T}. \tag{3.139}$$

We also see that in the case where the amount of substance in the system changes (i.e. when one more variable appears characterizing the state of the system, the amount of a substance in the system $G$), the expression for the total differential of the entropy of a simple system can be written in the following form:

$$dS=\left(\frac{\partial S}{\partial U}\right)_{V,\,G}dU+\left(\frac{\partial S}{\partial V}\right)_{U,\,G}dV+\left(\frac{\partial S}{\partial G}\right)_{U,\,V}dG. \tag{3.140}$$

Then, from (3.26) it is clear that

$$\left(\frac{\partial S}{\partial U}\right)_{V,\,G}=\frac{1}{T}, \tag{3.141}$$

and from (1.27) it follows that

$$\left(\frac{\partial S}{\partial V}\right)_{U,\,G}=\frac{p}{T}. \tag{3.142}$$

Combining these relations with (3.139), we find from (3.140) that

$$dS = \frac{1}{T}\,dU + \frac{p}{T}\,dV - \frac{\varphi}{T}\,dG, \tag{3.143}$$

or

$$T\,dS = dU + p\,dV - \varphi\,dG. \tag{3.144}$$

In a similar manner for a complex system we obtain

$$T\,dS = dU + p\,dV + \xi\,dW - \varphi^*\,dG. \tag{3.145}$$

For simple and complex systems, respectively, relations (3.142) and (3.143) represent the combined equation of the first and second laws of thermodynamics for systems with variable amount of substance.[3] Both are sometimes called the fundamental equation of Gibbs.

3.2.8. From (3.119) and (3.120) it is clear that the total differentials of the characteristic functions expressed through "their" variables (for the case when the amount of substance in the system changes) have the following form for simple systems:

$$dU = T\,dS - p\,dV + \varphi\,dG, \tag{3.146}$$

$$dH = T\,dS + V\,dp + \varphi\,dG, \tag{3.147}$$

$$dF = -S\,dT - p\,dV + \varphi\,dG, \tag{3.148}$$

$$d\Phi = -S\,dT + V\,dp + \varphi\,dG \tag{3.149}$$

and, respectively, for complex systems:

$$dU = T\,dS - p\,dV - \xi\,dW + \varphi^*\,dG, \tag{3.150}$$

$$dH^* = T\,dS + V\,dp + W\,d\xi + \varphi^*\,dG, \tag{3.151}$$

$$dF = -S\,dT - p\,dV - \xi\,dW + \varphi^*\,dG, \tag{3.152}$$

$$d\Phi^* = -S\,dT + V\,dp + W\,d\xi + \varphi^*\,dG. \tag{3.153}$$

3.2.9. Employing Legendre transformations (3.7), (3.4), and

$$\varphi\,dG = d\,(\varphi G) - G\,d\varphi \tag{3.154}$$

and assuming that in accordance with (3.42)

$$\Phi = \varphi G,$$

we can transform Eq. (3.144) to

$$d\,(TS) - S\,dT = dU + d\,(pV) - V\,dp - d\Phi + G\,d\varphi, \tag{3.155}$$

or, which is the same,

$$S\,dT - V\,dp + G\,d\varphi + d\,(U + pV - TS) - d\Phi = 0. \tag{3.156}$$

---

[3] We note that it is not obligatory to use the mass of a substance as a variable characterizing the amount of a substance in the system. In chemical thermodynamics a number of moles is usually used as such a variable.

From this and (3.13) it is obvious that

$$S\,dT - V\,dp + G\,d\varphi = 0. \tag{3.157}$$

This important thermodynamic relation is called the Gibbs-Duhem equation and is widely used in chemical thermodynamics.

In the same way we can easily obtain the Gibbs-Duhem equation for complex thermodynamic systems:

$$S\,dT - V\,dp - W\,d\xi + G\,d\varphi^* = 0. \tag{3.158}$$

3.2.10. We note that the relations obtained above, namely

$$\left(\frac{\partial u}{\partial G}\right)_{V,\,S} = \frac{pv - Ts}{G}, \tag{3.93}$$

$$\left(\frac{\partial h}{\partial G}\right)_{p,\,S} = -\frac{Ts}{G}, \tag{3.103}$$

$$\left(\frac{\partial f}{\partial G}\right)_{V,\,T} = \frac{pv}{G}, \tag{3.113}$$

$$\left(\frac{\partial s}{\partial G}\right)_{U,\,V} = -\frac{u + pv}{G}, \tag{3.136}$$

and their analogs for complex systems are, obviously, interesting in themselves: they show how the specific values of characteristic functions (and entropy) vary with the amount of substance in the corresponding thermodynamic systems.

## 3.3 The Massieu-Planck Functions

3.3.1. At one time it was suggested that characteristic functions other than $U$, $H$, $F$, and $\Phi$ should be introduced. But in thermodynamic calculations these functions are not used (for reasons considered below; see Sec. 3.3.7). Nevertheless, we find it expedient, from the pedagogical point of view to discuss these functions at least briefly.

3.3.2. It is easy to see that the method of introducing characteristic functions discussed in Sec. 3.1 was the same: we applied Legendre transformations (3.4), (3.7), and (3.48) to the combined equation of the first and second laws of thermodynamics written in form (1.27) or (1.30) (for simple or complex systems, respectively).

Somewhat different characteristic functions, usually called the *Massieu-Planck functions*, can be obtained if we apply the Legendre transformation to Eq. (1.27) in the following form:

$$dS = \frac{1}{T}\,dU + \frac{p}{T}\,dV. \tag{3.159}$$

Let us consider this relation.

(1) For a simple system in which $U$ and $V$ are constant (isolated system) there follows from (3.159) the well-known equilibrium condition (3.1a)

$$dS = 0.$$

Whence

$$\left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T} \tag{3.160}$$

and

$$\left(\frac{\partial S}{\partial V}\right)_U = \frac{p}{T}. \tag{3.161}$$

Entropy is a characteristic function if expressed in terms of $U$ and $V$, i.e. by finding the derivative of $S$ with respect to one of these variables and keeping the other constant we can find the values of $T$ and $p$ and, as a result, the values of $S$, $p$, $V$, $T$, and $U$. (The reader must bear in mind that entropy is not a thermodynamic potential.)

It is easy to see that if we combine Eq. (3.4) with (1.14) and (3.159), we find that

$$dS = \frac{1}{T}\, dH - \frac{V}{T}\, dp. \tag{3.162}$$

Hence it is clear that condition (3.1a)

$$dS = 0$$

will also be an equilibrium for such simple systems in which $H$ and $p$ are constant.

From (3.162) it follows that

$$\left(\frac{\partial S}{\partial H}\right)_p = \frac{1}{T} \tag{3.163}$$

and

$$\left(\frac{\partial S}{\partial p}\right)_H = -\frac{V}{T}. \tag{3.164}$$

Hence, entropy is a characteristic function if expressed in terms of $H$ and $p$.

Note that since entropy is a characteristic function of variables $U$ and $V$ and variables $H$ and $p$, it belongs to the group of Massieu-Planck functions.

(2) In accordance with (2.89) we may write

$$\frac{1}{T}\, dU = d\left(\frac{U}{T}\right) - U d\left(\frac{1}{T}\right), \tag{3.165}$$

which transforms (3.159) to

$$d\left(S - \frac{U}{T}\right) = -U d\left(\frac{1}{T}\right) + \frac{p}{T}\, dV. \tag{3.166}$$

Hence, for a simple isochoric-isothermal system ($V$ and $T$ constant) in equilibrium,

$$d\,(S - U/T) = 0. \tag{3.167}$$

We introduce the notation

$$\tilde{F} = S - U/T. \tag{3.168}$$

If we bear in mind (3.9), we find that

$$\tilde{F} = -F/T. \tag{3.169}$$

For an isochoric-isothermal system the function $\tilde{F}$ plays the same role as the isochoric-isothermal potential $F$. The function $\tilde{F}$ is sometimes called the *Massieu function*.[4] From (3.166) and (3.168) it follows that

$$\left(\frac{\partial \tilde{F}}{\partial \frac{1}{T}}\right)_V = -U \tag{3.170}$$

and

$$\left(\frac{\partial \tilde{F}}{\partial V}\right)_{1/T} = \frac{p}{T}. \tag{3.171}$$

It is then clear that $\tilde{F}$ is a characteristic function if expressed in terms of variables $V$ and $1/T$.

(3) Next, in accordance with (2.89) we can write

$$\frac{p}{T}\,dV = d\left(\frac{pV}{T}\right) - V d\left(\frac{p}{T}\right). \tag{3.172}$$

which transforms (3.166) to

$$d\left(S - \frac{U}{T} - \frac{pV}{T}\right) = -U d\left(\frac{1}{T}\right) - V d\left(\frac{p}{T}\right). \tag{3.173}$$

It is clear that for simple isobaric-isothermal systems ($p$ and $T$ constant) in equilibrium,

$$d\left(S - \frac{U}{T} - \frac{pV}{T}\right) = 0. \tag{3.174}$$

Let us introduce the notation

$$\tilde{\Phi} = S - \frac{U}{T} - \frac{pV}{T}. \tag{3.175}$$

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[4] F. Massieu was the first (1865) to apply the Legendre transformation to thermodynamic equations; he was also the first to formulate the relations known at present as the Gibbs-Helmholtz equations (see Sec. 5.2).

Equation (3.13) yields

$$\tilde{\Phi} = -\Phi/T. \tag{3.176}$$

It is obvious that for an isobaric-isothermal system the function $\tilde{\Phi}$ plays the same role as the usual isobaric-isothermal potential. The function $\tilde{\Phi}$ is often called the *Planck function.*

From (3.173) and (3.176) it follows that

$$\left(\frac{\partial\tilde{\Phi}}{\partial\frac{1}{T}}\right)_{p/T} = -U \tag{3.177}$$

and

$$\left(\frac{\partial\tilde{\Phi}}{\partial\frac{p}{T}}\right)_{1/T} = -V. \tag{3.178}$$

We see that the Planck function is a characteristic function if expressed in terms of $p/T$ and $1/T$.

Since, naturally,

$$d\left(\frac{p}{T}\right) = \frac{1}{T}\,dp + p\,d\left(\frac{1}{T}\right), \tag{3.179}$$

Eq. (3.173) in accordance with (3.176) can be written in the following form:

$$d\tilde{\Phi} = -U d\left(\frac{1}{T}\right) - \frac{V}{T}\,dp - pV\,d\left(\frac{1}{T}\right). \tag{3.180}$$

Bearing in mind (1.14), we obtain

$$d\tilde{\Phi} = -H d\left(\frac{1}{T}\right) - \frac{V}{T}\,dp. \tag{3.181}$$

From this it follows that

$$\left(\frac{\partial\tilde{\Phi}}{\partial\frac{1}{T}}\right)_{p} = -H \tag{3.182}$$

and

$$\left(\frac{\partial\tilde{\Phi}}{\partial p}\right)_{1/T} = -\frac{V}{T}. \tag{3.183}$$

Therefore, the Planck function is a characteristic function if expressed in terms of $p$ and $1/T$.

(4) Finally, if we substitute (3.172) into (3.159), we get

$$d\left(S - \frac{pV}{T}\right) = \frac{1}{T}\,dU - V\,d\left(\frac{p}{T}\right). \tag{3.184}$$

From this it is clear that for a simple thermodynamic system in which $U$ and $p/T$ are constant, in a state of equilibrium,

$$d\left(S-\frac{pV}{T}\right)=0. \tag{3.185}$$

Let us introduce the notation

$$I=S-\frac{pV}{T}, \tag{3.186}$$

or, which is the same,

$$I=\frac{TS-pV}{T}. \tag{3.186a}$$

From (3.13) it follows that

$$I=-\frac{\Phi-U}{T}. \tag{3.187}$$

As we can see from (3.184),

$$\left(\frac{\partial I}{\partial U}\right)_{p/T}=\frac{1}{T} \tag{3.188}$$

and

$$\left(\frac{\partial I}{\partial\frac{p}{T}}\right)_{U}=-V. \tag{3.189}$$

Therefore, $I$ is a characteristic function if expressed in terms of $U$ and $p/T$. Indeed, if we find the value of $T$ with the help of (3.188) and know $p/T$, we can find $p$; if then we find $V$ with the help of (3.189) and knowing $p$ and $T$, we can find $S$ from (3.186); etc.

We should like to stress, however, that the function $I$ is of purely pedagogical interest. It has no practical application due to the complex conditions in which the system must couple with the surroundings (besides $U$ being constant, the condition $p/T$ = const must be fulfilled, too).

3.3.3. Let us introduce the notion of the specific values of the Massieu-Planck functions:

$$\tilde{f}=\frac{\tilde{F}}{G}, \tag{3.190}$$

$$\tilde{\varphi}=\frac{\tilde{\Phi}}{G}, \tag{3.191}$$

and

$$i=\frac{I}{G}. \tag{3.192}$$

If we combine these relations with (3.168), (3.175), and (3.186), we find that

$$\tilde{f} = s - u/T, \tag{3.193}$$

$$\tilde{\varphi} = s - pv/T, \tag{3.194}$$

$$i = s - pv/T. \tag{3.195}$$

Further, from (3.190), (3.169), and (3.40) it is clear that

$$\tilde{f} = -f/T, \tag{3.196}$$

and from (3.191), (3.176), and (3.42) that

$$\tilde{\varphi} = -\varphi/T. \tag{3.197}$$

Obviously, if the amount of substance in the system remains unchanged ($G = \text{const}$), (3.160) and (3.161) can be represented in the following form:

$$\left(\frac{\partial s}{\partial u}\right)_v = \frac{1}{T} \tag{3.160a}$$

and

$$\left(\frac{\partial s}{\partial v}\right)_u = \frac{p}{T} \tag{3.161a}$$

(see relations (3.133) and (3.132)); relations (3.166), (3.170), and (3.171) can be represented in the form

$$d\tilde{f} = -u d\left(\frac{1}{T}\right) + \frac{p}{T} dv, \tag{3.166a}$$

$$\left(\frac{\partial \tilde{f}}{\partial \frac{1}{T}}\right)_v = -u, \tag{3.170a}$$

$$\left(\frac{\partial \tilde{f}}{\partial v}\right)_{1/T} = \frac{p}{T}; \tag{3.171a}$$

relations (3.172), (3.177), and (3.178) in the form

$$d\tilde{\varphi} = -u d\left(\frac{1}{T}\right) - v d\left(\frac{p}{T}\right), \tag{3.172a}$$

$$\left(\frac{\partial \tilde{\varphi}}{\partial \frac{1}{T}}\right)_{p/T} = -u, \tag{3.177a}$$

$$\left(\frac{\partial \tilde{\varphi}}{\partial \frac{p}{T}}\right)_{1/T} = -v, \tag{3.178a}$$

and relations (3.184), (3.188), and (3.189) in the form

$$di=\frac{1}{T}\,du-v\,d\left(\frac{p}{T}\right), \tag{3.184a}$$

$$\left(\frac{\partial i}{\partial u}\right)_{p/T}=\frac{1}{T}, \tag{3.188a}$$

$$\left(\frac{\partial i}{\partial \frac{p}{T}}\right)_{u}=-v. \tag{3.189a}$$

3.3.4. If we use a method analogous to that applied in Sec. 3.2, we can easily show that

$$\left(\frac{\partial S}{\partial G}\right)_{U,\,V}=\left(\frac{\partial \tilde F}{\partial G}\right)_{V,\,1/T}=\left(\frac{\partial \tilde\Phi}{\partial G}\right)_{p/T,\,1/T}=\left(\frac{\partial I}{\partial G}\right)_{U,\,p/T}=\tilde\varphi. \tag{3.198}$$

We will recall that we have already obtained relation (3.138)

$$\left(\frac{\partial S}{\partial G}\right)_{U,\,V}=-\frac{\varphi}{T},$$

which, together with (3.197)

$$\tilde\varphi=-\frac{\varphi}{T},$$

is equivalent to (3.198). We are not surprised, naturally, that variation of these characteristic functions with the amount of substance in the system is related to the value of the chemical potential $\varphi$.

3.3.5. If we consider (3.198), we find that the total differentials of these characteristic functions, expressed in terms of their "own" variables, for the case where the amount of substance in the system varies, have the following form:

$$dS=\frac{1}{T}\,dU+\frac{p}{T}\,dV+\tilde\varphi\,dG \tag{3.199}$$

(this relation is, obviously, equivalent to (3.143)),

$$d\tilde F=-U\,d\left(\frac{1}{T}\right)+\frac{p}{T}\,dV+\tilde\varphi\,dG, \tag{3.200}$$

$$d\tilde\Phi=-U\,d\left(\frac{1}{T}\right)-V\,d\left(\frac{p}{T}\right)+\tilde\varphi\,dG, \tag{3.201}$$

$$dI=\frac{1}{T}\,dU-V\,d\left(\frac{p}{T}\right)+\tilde\varphi\,dG. \tag{3.202}$$

Since, naturally,

$$d\left(\frac{p}{T}\right)=\frac{1}{T}\,dp+p\,d\frac{1}{T}, \tag{3.203}$$

Eq. (3.201) combined with (1.14) can also be represented in the following form:

$$d\tilde{\Phi} = -H d\left(\frac{1}{T}\right) - \frac{V}{T} dp + \tilde{\varphi} dG. \qquad (3.204)$$

3.3.6. We introduce the Planck function and the function $I$ for complex thermodynamic systems along the same lines. Let us write Eq. (1.30) in the form

$$dS = \frac{1}{T} dU + \frac{p}{T} dV + \frac{\xi}{T} dW, \qquad (3.205)$$

and consider how this equation can be transformed for four types of conditions of interaction of a complex system with the surrounding medium, the conditions discussed in Sec. 3.3.2 for a simple system.

(1) For a complex system with $U$, $V$, and $W$ constant (an isolated system), it is obvious from (3.205) that condition (3.1a) is valid just as for a simple isolated system. From (3.205) it follows that

$$\left(\frac{\partial S}{\partial U}\right)_{V, W} = \frac{1}{T}, \qquad (3.206)$$

$$\left(\frac{\partial S}{\partial V}\right)_{U, W} = \frac{p}{T}, \qquad (3.207)$$

$$\left(\frac{\partial S}{\partial W}\right)_{U, V} = \frac{\xi}{T}. \qquad (3.208)$$

(2) Bearing in mind (3.165), we can transform Eq. (3.205) to

$$d\left(S - \frac{U}{T}\right) = -U d\left(\frac{1}{T}\right) + \frac{p}{T} dV + \frac{\xi}{T} dW, \qquad (3.209)$$

or, bearing in mind (3.168),

$$d\tilde{F} = -U d\left(\frac{1}{T}\right) + \frac{p}{T} dV + \frac{\xi}{T} dW. \qquad (3.210)$$

Hence, it is clear that for a complex system with $1/T$, $V$, and $W$ constant in the equilibrium state

$$d\tilde{F} = 0. \qquad (3.211)$$

Thus, the expressions for the Massieu function are identical for complex and simple systems (3.168)-(3.169) (relations (3.193) and (3.196) for mass specific quantities), just as the expressions for the isochoric-isothermal potential $F$, (3.9) and (3.41), are identical for simple and complex systems.

From (3.210) it also follows that

$$\left(\frac{\partial\tilde{F}}{\partial\frac{1}{T}}\right)_{V,\,W}=-U, \tag{3.212}$$

$$\left(\frac{\partial\tilde{F}}{\partial V}\right)_{1/T,\,W}=\frac{p}{T}, \tag{3.213}$$

and

$$\left(\frac{\partial\tilde{F}}{\partial W}\right)_{1/T,\,V}=\frac{\xi}{T}. \tag{3.214}$$

(3) In accordance with (2.89) we may write

$$\frac{\xi}{T}\,dW=d\left(\frac{\xi W}{T}\right)-Wd\left(\frac{\xi}{T}\right). \tag{3.215}$$

Using (3.172) and (3.215), we can transform Eq. (3.209) to

$$d\left(S-\frac{U}{T}-\frac{pV}{T}-\frac{\xi W}{T}\right)=-Ud\left(\frac{1}{T}\right)-Vd\left(\frac{p}{T}\right)-Wd\left(\frac{\xi}{T}\right). \tag{3.216}$$

Let us introduce the notation

$$\tilde{\Phi}^*=S-\frac{U}{T}-\frac{pV}{T}-\frac{\xi W}{T}. \tag{3.217}$$

From (3.59) it is clear that

$$\tilde{\Phi}^*=-\Phi^*/T. \tag{3.218}$$

In terms of specific quantities these relations can be written thus:

$$\tilde{\varphi}^*=s-\frac{u}{T}-\frac{pv}{T}-\frac{\xi w}{T} \tag{3.217a}$$

and

$$\tilde{\varphi}^*=-\varphi^*/T. \tag{3.218a}$$

Bearing in mind (3.218), we can write (3.216) in the form

$$d\tilde{\Phi}^*=-Ud\left(\frac{1}{T}\right)-Vd\left(\frac{p}{T}\right)-Wd\left(\frac{\xi}{T}\right). \tag{3.219}$$

For a complex system with $1/T$, $p/T$, and $\xi/T$ constant (i.e., to put it simply, $T$, $p$, and $\xi$ are kept constant), in the equilibrium state,

$$d\tilde{\Phi}^*=0. \tag{3.220}$$

From (3.219) it follows that

$$\left(\frac{\partial \tilde{\Phi}^*}{\partial \frac{1}{T}}\right)_{p/T,\ \xi/T} = -U, \tag{3.221}$$

$$\left(\frac{\partial \tilde{\Phi}^*}{\partial \frac{p}{T}}\right)_{1/T,\ \xi/T} = -V, \tag{3.222}$$

and

$$\left(\frac{\partial \tilde{\Phi}^*}{\partial \frac{\xi}{T}}\right)_{1/T,\ p/T} = -W. \tag{3.223}$$

(4) Finally, if we transform Eq. (3.205) by employing (3.172) and (3.215), we obtain

$$d\left(S-\frac{pV}{T}-\frac{\xi W}{T}\right)=\frac{1}{T}\,dU-Vd\left(\frac{p}{T}\right)-Wd\left(\frac{\xi}{T}\right). \tag{3.224}$$

If we introduce the notation

$$I^* = S-\frac{pV}{T}-\frac{\xi W}{T}, \tag{3.225}$$

or, which is the same,

$$I^* = \frac{TS-pV-\xi W}{T}, \tag{3.225a}$$

then from (3.5a) we see that

$$I^* = -\frac{\Phi^*-U}{T}. \tag{3.226}$$

In terms of specific quantities these relations are, naturally, of the following form:

$$i^* = s-\frac{pv}{T}-\frac{\xi w}{T} \tag{3.225b}$$

and

$$i^* = -\frac{\varphi^*-u}{T}. \tag{3.226a}$$

Using the new notation, we can write (3.224) in the following form:

$$dI^* = \frac{1}{T}\,dU-Vd\left(\frac{p}{T}\right)-Wd\left(\frac{\xi}{T}\right). \tag{3.227}$$

It is clear that for a complex system with $U$, $p/T$, and $\xi/T$ constant, in the equilibrium state,

$$dI^* = 0. \tag{3.228}$$

Equation (3.227) implies that

$$\left(\frac{\partial I^*}{\partial U}\right)_{p/T,\,\xi/T}=\frac{1}{T}, \tag{3.229}$$

$$\left(\frac{\partial I^*}{\partial \frac{p}{T}}\right)_{U,\,\xi/T}=-V, \tag{3.230}$$

and

$$\left(\frac{\partial I^*}{\partial \frac{\xi}{T}}\right)_{U,\,p/T}=-W. \tag{3.231}$$

3.3.7. As pointed out above, the functions $\tilde{F}$ and $\tilde{\Phi}$ are not used in thermodynamic calculations (except for some problems involving irreversible processes). They were the first characteristic functions that Massieu introduced into thermodynamics. Planck in his works often used the function $\tilde{\Phi}$. The modern, so to say, characteristic functions (enthalpy and the isochoric-isothermal and isobaric-isothermal potentials) came into use considerably later than the Massieu-Planck functions.

The characteristic functions $U$, $H$, $F$, and $\Phi$ have an important advantage over the Massieu-Planck characteristic functions—they are thermodynamic potentials. We recall (see Sec. 3.1.3) that for a quantity to be a thermodynamic potential the work $L^*$ that a complex system can perform under given conditions of coupling with the surrounding medium is equal to the decrease in the corresponding characteristic function (see Eqs. (3.18a) through (3.21a)). The Massieu-Planck functions do not possess these properties. This can easily be shown.

From Eq. (1.29)

$$T\,dS = dU + p\,dV + dL^*$$

it follows that for a complex system with $U$ and $V$ constant,

$$dL^* = T\,dS. \tag{3.232}$$

Next, we write (1.29) in the following form:

$$dS=\frac{1}{T}\,dU+\frac{p}{T}\,dV+\frac{1}{T}\,dL^*. \tag{3.233}$$

Taking into account (3.165) and (3.168), we transform this equation to

$$d\tilde{F}=-U d\left(\frac{1}{T}\right)+\frac{p}{T}\,dV+\frac{1}{T}\,dL^*, \tag{3.234}$$

whence for a complex isochoric-isothermal system

$$dL^* = T\,d\tilde{F}. \tag{3.235}$$

In the system under consideration $T$ is constant and, therefore, if we use (3.169), we find from (3.235) that

$$dL^* = -\,dF. \tag{3.235a}$$

This result is obvious *a priori*, since we are speaking of the same isochoric-isothermal system for which we earlier obtained relation (3.20a).

If we combine (3.165) and (3.172), we can transform Eq. (3.233) to

$$d\left(S-\frac{U}{T}-\frac{pV}{T}\right)=-U\,d\left(\frac{1}{T}\right)-V\,d\left(\frac{p}{T}\right)+\frac{1}{T}\,dL^*. \tag{3.236}$$

or, with due regard for (3.175),

$$d\tilde{\Phi}=-U\,d\left(\frac{1}{T}\right)-V\,d\left(\frac{p}{T}\right)+\frac{1}{T}\,dL^*, \tag{3.237}$$

We see that for a complex isobaric-isothermal system,

$$dL^* = T\,d\tilde{\Phi}. \tag{3.238}$$

Since in this system $T$ is kept constant, it is evident from this relation and (3.176) that

$$dL^* = -\,d\Phi, \tag{3.238a}$$

which is an obvious result for isobaric-isothermal systems (see (3.21a)).

Finally, if we use only (3.172) to transform (3.233), we obtain

$$d\left(S-\frac{pV}{T}\right)=\frac{1}{T}\,dU-V\,d\left(\frac{p}{T}\right)+\frac{1}{T}\,dL^*, \tag{3.239}$$

i.e. with due regard for (3.186),

$$dI=\frac{1}{T}\,dU-V\,d\left(\frac{p}{T}\right)+\frac{1}{T}\,dL^*. \tag{3.240}$$

Hence, it follows that for a complex system with $U$ and $p/T$ constant,

$$dL^* = T\,dI. \tag{3.241}$$

From Eqs. (3.232), (3.235), (3.238), and (3.241) which we have just derived it can be seen that the work $L^*$ is not done at the expense of the corresponding characteristic function (as it was in the cases of the main characteristic functions discussed in Sec. 3.1; see Eqs. (3.18a)-(3.21a)).

Consequently, the Massieu-Planck functions $S$, $\tilde{F}$, $\tilde{\Phi}$, and $I$ do not, indeed, possess the properties of a thermodynamic potential.[5]

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[5] The reader must not be misled by relations (3.235a) and (3.238a): the characteristic function for the variables $1/T$ and $V$ is $\tilde{F}$ and not $F$, while that for the variables $1/T$ and $p/T$ is $\tilde{\Phi}$ and not $\Phi$.

We will mention the Massieu-Planck functions once more in Sec. 5.2.

3.3.8. Concerning the Massieu-Planck functions it is in place to make the following remark.

Equation (3.199)

$$dS = \frac{1}{T}\,dU + \frac{p}{T}\,dV + \tilde{\varphi}\,dG,$$

combined with Legendre transformations (3.165), (3.172), and

$$\tilde{\varphi}\,dG = d\,(\tilde{\varphi}G) - G d\,\tilde{\varphi}, \tag{3.242}$$

and with due regard for (3.191), which states that

$$\tilde{\varphi}G = \tilde{\Phi},$$

can be written thus:

$$dS = d\left(\frac{U}{T}\right) - U d\left(\frac{1}{T}\right) + d\left(\frac{pV}{T}\right) - V d\left(\frac{p}{T}\right) + d\tilde{\Phi} - G\,d\tilde{\varphi}. \tag{3.243}$$

Whence, using (3.175), we obtain

$$U d\left(\frac{1}{T}\right) + V d\left(\frac{p}{T}\right) - G\,d\tilde{\varphi} = 0. \tag{3.244}$$

This is simply another way of presenting the Gibbs-Duhem equation (3.157) discussed above.

3.3.9. To conclude the discussion of the Massieu-Planck characteristic functions we will make one more, purely pedagogical, remark.

The main characteristic functions $U$, $H$, $F$, and $\Phi$ were introduced by applying Legendre transformations to Eq. (3.25)

$$dU = T\,dS - p\,dV$$

for four variables: $V$ and $S$, $p$ and $S$, $V$ and $T$, and $p$ and $T$. For obvious reasons there is no point in discussing two more possible pairs, $V$ and $p$, and $T$ and $S$.

The method of introducing the Massieu-Planck functions was, generally, the same—we applied Legendre transformations to Eq. (3.159)

$$dS = \frac{1}{T}\,dU - \frac{p}{T}\,dV$$

for four pairs of variables: $V$ and $U$, $p/T$ and $U$, $V$ and $1/T$, and $p/T$ and $1/T$. There is no point in discussing pairs $V$ and $p/T$, and $1/T$ and $U$. (Sometimes in thermodynamics courses Eq. (3.25) is called the combined equation of the first and second laws of thermodynamics in terms of energy and Eq. (3.159) the combined equation in terms of entropy.) The same classification can be introduced for Eqs. (3.62) and (3.205) for complex systems.

## 3.4 The Grand Potential and the Kramers Function

3.4.1. Let us consider the combined equation of the first and second laws of thermodynamics for systems with a variable amount of substance (3.144):

$$T\,dS = dU + p\,dV - \varphi\,dG.$$

If to this equation we apply Legendre transformations (3.7)

$$T\,dS = d\,(TS) - S\,dT$$

and (3.154)

$$\varphi\,dG = d\,(\varphi G) - G\,d\varphi,$$

and bear in mind that in accordance with (3.42)

$$\Phi - \varphi G,$$

we obtain

$$d\,(U - TS - \Phi) = -S\,dT - p\,dV - G\,d\varphi. \qquad (3.245)$$

It is clear that for a simple system with $T$, $V$, and $\varphi$ constant,

$$d\,(U - TS - \Phi) = 0. \qquad (3.246)$$

Let us introduce the notation

$$\Gamma = U - TS - \Phi. \qquad (3.247)$$

If we take (3.9) and (3.13) into account, we have

$$\Gamma = F - \Phi, \qquad (3.248)$$

or, which is the same,

$$\Gamma = -pV, \qquad (3.249)$$

The function $\Gamma$ is usually called the *grand potential*.

By virtue of (3.247) we can write (3.245) as

$$d\Gamma = -S\,dT - p\,dV - G\,d\varphi. \qquad (3.250)$$

It follows then that

$$\left(\frac{\partial \Gamma}{\partial T}\right)_{V,\,\varphi} = -S, \qquad (3.251)$$

$$\left(\frac{\partial \Gamma}{\partial V}\right)_{T,\,\varphi} = -p, \qquad (3.252)$$

and

$$\left(\frac{\partial \Gamma}{\partial \varphi}\right)_{V,\,T} = -G. \qquad (3.253)$$

From the above relations it is clear that if the grand potential is expressed in terms of $V$, $T$, and $\varphi$, it is a characteristic function.

Indeed, the values of $T$ and $V$ are given, $p$ is determined from (3.252); if $\varphi$ is known, having found $G$ from (3.253) we can find $\Phi$ and by the value of $S$ known from (3.251) and the values of $p$, $V$, $T$, and $\Phi$ we can determine $U$; and so on.

3.4.2. The concept of the grand potential for complex systems is introduced in a similar manner. From the combined equation of the first and second laws of thermodynamics for a complex system with a variable amount of substance, (3.145)

$$T\,dS = dU + p\,dV + \xi\,dW - \varphi^*\,dG,$$

using Legendre transformations (3.7) and

$$\varphi^*\,dG = d(\varphi^* G) - G\,d\varphi^* \tag{3.154a}$$

and taking into account (3.42a), we obtain

$$d\Gamma^* = -S\,dT - p\,dV - \xi\,dW - G\,d\varphi^*, \tag{3.254}$$

where

$$\Gamma^* = U - TS - \Phi^*, \tag{3.255}$$

or, which is the same,

$$\Gamma^* = F - \Phi^* \tag{3.256}$$

and

$$\Gamma^* = -pV - \xi W. \tag{3.257}$$

From (3.254) it is clear that for a complex system in which $T$, $V$, $W$, and $\varphi^*$ are constant, in a state of equilibrium,

$$d\Gamma^* = 0. \tag{3.258}$$

The function $\Gamma^*$ is the grand potential for a complex system.

From (3.254) we see that

$$\left(\frac{\partial \Gamma^*}{\partial V}\right)_{T,\,W,\,\varphi^*} = -p, \tag{3.259}$$

$$\left(\frac{\partial \Gamma^*}{\partial W}\right)_{T,\,V,\,\varphi^*} = -\xi, \tag{3.260}$$

$$\left(\frac{\partial \Gamma^*}{\partial T}\right)_{V,\,W,\,\varphi^*} = -S, \tag{3.261}$$

and

$$\left(\frac{\partial \Gamma^*}{\partial \varphi^*}\right)_{T,\,V,\,W} = -G. \tag{3.262}$$

3.4.3. The characteristic function $\Gamma^*$ has the properties of a thermodynamic potential. Indeed, if we take into account Eq. (1.7), we can write (3.145) as

$$T\,dS = dU + p\,dV + dL^* - \varphi^*\,dG, \tag{3.263}$$

and using (3.7) and (3.154a), we can transform it to

$$d\Gamma^* = -S\,dT - p\,dV - G\,d\varphi^* - dL^*. \tag{3.264}$$

Hence, it follows that for a complex thermodynamic system in which $T$, $V$, and $\varphi^*$ are constant we have

$$dL^* = -d\Gamma^*, \tag{3.265}$$

i.e. under given conditions of interaction with the surrounding medium a system of this type performs work $L^*$ at the expense of the characteristic function $\Gamma^*$.

It is interesting to note that while in the case of the common thermodynamic potentials ($H$ and $\Phi$), under appropriate conditions of coupling with the surroundings a complex system performs work at the expense of the corresponding potential of a simple system: $dL^* = -dH$ and $dL^* = -d\Phi$ (this is seen from Eqs. (3.19a) and (3.21a), in the given case the work $L^*$ is performed at the expense not of the "simple" grand potential $\Gamma$ but of the complex grand potential $\Gamma^*$. This is not surprising since in Sec. 3.1.3 for a complex system with a constant amount of substance we used Eq. (1.29), while here we use Eq. (3.145) containing besides $L^*$ the quantity $\varphi^*$, due to which in (3.264) and (3.265) there appears $\Gamma^*$ instead of $\Gamma$. At the same time it is obvious from (3.157) that $\Gamma$ is not a thermodynamic potential (since for the complex system under consideration $dL^* \neq d\Gamma$).

3.4.4. The grand potential is widely used in statistical thermodynamics for calculating the grand canonical ensemble. In classical thermodynamics the grand potential is not used.

3.4.5. If we write Eq. (3.144) in the form

$$dS = \frac{1}{T}\,dU + \frac{p}{T}\,dV - \frac{\varphi}{T}\,dG \tag{3.266}$$

and employ Legendre transformations (3.165)

$$\frac{1}{T}\,dU = d\left(\frac{U}{T}\right) - U d\left(\frac{1}{T}\right),$$

and

$$\frac{\varphi}{T}\,dG = d\left(\frac{\varphi G}{T}\right) - G d\left(\frac{\varphi}{T}\right), \tag{3.267}$$

then, using (3.42), we can write (3.266) in the following form:

$$d\left(S - \frac{U}{T} + \frac{\Phi}{T}\right) = -U d\left(\frac{1}{T}\right) + \frac{p}{T}\,dV + G d\left(\frac{\varphi}{T}\right). \tag{3.268}$$

It is clear that for a simple system in which $T$, $V$, and $\varphi/T$ are constant (and since $T$ is constant, $\varphi$ is constant, too),

$$d\left(S - \frac{U}{T} + \frac{\Phi}{T}\right) = 0. \tag{3.269}$$

We introduce the notation

$$\tilde{\Gamma}=S-\frac{U}{T}+\frac{\Phi}{T}. \qquad (3.270)$$

If we combine (3.247) and this relation, we see that

$$\tilde{\Gamma}=-\Gamma/T. \qquad (3.271)$$

The quantity $\tilde{\Gamma}$ is usually called the Kramers function.

Bearing in mind (3.270), we can write Eq. (3.268) in the following form:

$$d\tilde{\Gamma}=-Ud\left(\frac{1}{T}\right)+\frac{p}{T}dV+Gd\left(\frac{\varphi}{T}\right), \qquad (3.272)$$

or, using (3.197),

$$d\tilde{\Gamma}=-Ud\left(\frac{1}{T}\right)+\frac{p}{T}dV-G\,d\tilde{\varphi}. \qquad (3.273)$$

From (3.272) it is evident that

$$\frac{\partial\tilde{\Gamma}}{\left(\partial\frac{1}{T}\right)_{V,\,\varphi/T}}=-U, \qquad (3.274)$$

$$\left(\frac{\partial\tilde{\Gamma}}{\partial V}\right)_{1/T,\,\varphi/T}=\frac{p}{T}, \qquad (3.275)$$

and

$$\left(\frac{\partial\tilde{\Gamma}}{\partial\frac{\varphi}{T}}\right)_{1/T,\,V}=G. \qquad (3.276)$$

From the above relations it follows that the Kramers function is a characteristic function if expressed in terms of $V$, $1/T$, and $\varphi/T$.

In the same way we can introduce the Kramers function for complex systems. If we write Eq. (3.145) in the form

$$dS=\frac{1}{T}dU+\frac{p}{T}dV+\frac{\xi}{T}dW-\frac{\varphi^*}{T}dG \qquad (3.277)$$

and apply Legendre transformations (3.165) and

$$\frac{\varphi^*}{T}dG=d\left(\frac{\varphi^*G}{T}\right)-Gd\left(\frac{\varphi^*}{T}\right), \qquad (3.278)$$

using (3.42a), we find from (3.277) that

$$d\tilde{\Gamma}^*=-Ud\left(\frac{1}{T}\right)+\frac{p}{T}dV+\frac{\xi}{T}dW+Gd\left(\frac{\varphi^*}{T}\right), \qquad (3.279)$$

or, bearing in mind (3.218a)

$$d\tilde{\Gamma}^*=-Ud\left(\frac{1}{T}\right)+\frac{p}{T}dV+\frac{\xi}{T}dW-G\,d\tilde{\varphi}^*. \qquad (3.280)$$

Here

$$\tilde{\Gamma}^* = S - \frac{U}{T} + \frac{\Phi^*}{T}, \tag{3.281}$$

or, according to (3.226),

$$\tilde{\Gamma}^* = -\Gamma^*/T. \tag{3.282}$$

It is obvious that for a complex system with $T$, $V$, $W$, and $\varphi^*$ constant, in the equilibrium state,

$$d\tilde{\Gamma}^* = 0. \tag{3.283}$$

From (3.279) we see that

$$\left(\frac{\partial \tilde{\Gamma}^*}{\partial \frac{1}{T}}\right)_{V,\, W,\, \varphi^*/T} = -U, \tag{3.284}$$

$$\left(\frac{\partial \tilde{\Gamma}^*}{\partial V}\right)_{1/T,\, W,\, \varphi^*/T} = \frac{p}{T}, \tag{3.285}$$

$$\left(\frac{\partial \tilde{\Gamma}^*}{\partial W}\right)_{1/T,\, V,\, \varphi^*/T} = \frac{\xi}{T}, \tag{3.286}$$

and

$$\left(\frac{\partial \tilde{\Gamma}^*}{\partial \frac{\varphi^*}{T}}\right)_{1/T,\, V,\, W} = G. \tag{3.287}$$

We can easily show that the Kramers function is not a thermodynamic potential. Substituting $\xi dW$ in Eq. (3.279) with the help of (1.7), we get

$$d\tilde{\Gamma}^* = -Ud\left(\frac{1}{T}\right) + \frac{p}{T}dV + Gd\left(\frac{\varphi^*}{T}\right) + \frac{1}{T}dL^*. \tag{3.288}$$

It is obvious that for the system under consideration, with $V$, $T$, and $\varphi^*$ constant,

$$dL^* = T\, d\tilde{\Gamma}^*. \tag{3.289}$$

Since in this system $T$ is constant, using (3.282) we can write (3.289) in the following form:

$$dL^* = -d\Gamma^*, \tag{3.289a}$$

which is obvious *a priori*.

We see that the work $L^*$ is performed not at the expense of the corresponding function $\tilde{\Gamma}^*$; therefore, $\tilde{\Gamma}^*$ does not have the properties of a thermodynamic potential. It is obvious that the Kramers function $\tilde{\Gamma}$ is related to the grand potential $\Gamma$ in the same manner as the Massieu-Planck functions are related to the main characteristic functions ($U$, $H$, $F$, and $\Phi$). The Kramers function is not widely applied in thermodynamic calculations.

## 3.5 Other Characteristic Functions

3.5.1. As we saw in Sec. 3.4.1, the grand potential $\Gamma$ was introduced by using in Eq. (3.144)

$$T\,dS = dU + p\,dV - \varphi\,dG$$

Legendre transformations (3.7) for the quantity $T\,dS$ and (3.154) for $\varphi\,dG$. Earlier, in Sec. 3.2.9, we saw that if we apply the Legendre transformation (3.4) together with (3.7) and (3.154) to $p\,dV$, then Eq. (3.144) is transformed into the Gibbs-Duhem equation.

Thus, in the first case, in Eq. (3.144) we used the transformation for the quantity $T\,dS$ in addition to transformation (3.154) for $\varphi\,dG$, while in the second case we used transformations both for $T\,dS$ and $p\,dV$. In both cases, when considering Eq. (3.144) the characteristic feature is the application of transformation (3.154) to $\varphi\,dG$.

We can also easily see that if we must use transformation (3.154), there are two more ways in which we can handle Eq. (3.144): (1) using neither transformation (3.7) nor transformation (3.4), and (2) using only transformation (3.4). Treating Eq. (3.144) along the same lines results in two more interesting characteristic functions.

3.5.2. Let us perform the required transformations.

(1) If in Eq. (3.144)

$$T\,dS = dU + p\,dV - \varphi\,dG$$

we substitute the quantity $\varphi\,dG$ with the help of (3.154)

$$\varphi\,dG = d(\varphi G) - G\,d\varphi$$

and take into account (3.42), we obtain

$$d(U - \Phi) = T\,dS - p\,dV - G\,d\varphi. \tag{3.290}$$

It is clear that for a simple system in which $S$, $V$, and $\varphi$ are constant, in the equilibrium state,

$$d(U - \Phi) = 0. \tag{3.291}$$

Let us introduce the notation

$$\Pi = U - \Phi. \tag{3.292}$$

This combined with (3.13) yields

$$\Pi = TS - pV. \tag{3.293}$$

Using this notation, we can write (3.290) in the following form:

$$d\Pi = T\,dS - p\,dV - G\,d\varphi. \tag{3.294}$$

Hence it is clear that

$$\left(\frac{\partial \Pi}{\partial S}\right)_{V,\,\varphi} = T, \tag{3.295}$$

$$\left(\frac{\partial \Pi}{\partial V}\right)_{S,\,\varphi} = -p, \tag{3.296}$$

and

$$\left(\frac{\partial \Pi}{\partial \varphi}\right)_{S,\,V} = -G. \tag{3.297}$$

From these relations it follows that Π is a characteristic function if expressed in terms of $S$, $V$, and $\varphi$.

In the same way a similar characteristic function can be introduced for a complex system: transforming Eq. (3.145) with the help of (3.154a), we obtain

$$d\Pi^* = T\,dS - p\,dV - \xi\,dW - G\,d\varphi^*, \tag{3.298}$$

where

$$\Pi^* = U - \Phi^*, \tag{3.299}$$

or, which is the same,

$$\Pi^* = TS - pV - \xi W. \tag{3.300}$$

From (3.298) it follows that for a complex system in which $S$, $V$, $W$, and $\varphi^*$ are constant, in the equilibrium state,

$$d\Pi^* = 0. \tag{3.301}$$

From (3.298) it follows that

$$\left(\frac{\partial \Pi^*}{\partial S}\right)_{V,\,W,\,\varphi^*} = T, \tag{3.302}$$

$$\left(\frac{\partial \Pi^*}{\partial V}\right)_{S,\,W,\,\varphi^*} = -p, \tag{3.303}$$

$$\left(\frac{\partial \Pi^*}{\partial W}\right)_{S,\,V,\,\varphi^*} = -\xi, \tag{3.304}$$

and

$$\left(\frac{\partial \Pi^*}{\partial \varphi^*}\right)_{S,\,V,\,W} = -G. \tag{3.305}$$

It is easy to show that the characteristic function $\Pi^*$ is a thermodynamic potential: if we substitute in (3.298) the quantity $\xi\,dW$ using (1.7), we obtain

$$d\Pi^* = T\,dS - p\,dV - G\,d\varphi^* - dL^*. \tag{3.306}$$

Hence, it is obvious that for a complex thermodynamic system in which $S$, $V$, and $\varphi^*$ are constant

$$dL^* = -d\Pi^*, \tag{3.307}$$

i.e. under the given conditions of interaction with the surrounding medium the work $L^*$ that such a system can perform is only at the expense of the characteristic function $\Pi^*$. At the same time it is obvious from (3.307) that $\Pi$ is not a thermodynamic potential (since $dL^* \neq -d\Pi$).

Note that the functions $\Pi$ and $\Pi^*$ considered here are uniquely related to the functions $I$ and $I^*$ introduced earlier in Sec. 3.3. Indeed, comparing relations (3.186a) and (3.293), we see that

$$\Pi = TI, \tag{3.308}$$

while comparing relations (3.225a) and (3.300) we see that

$$\Pi^* = TI^*. \tag{3.309}$$

(2) If in (3.144) we substitute the quantity $\varphi\, dG$ using (3.154) and the quantity $p\, dV$ using (3.4) and take into account (3.42), we obtain

$$d(U + pV - \Phi) = T\, dS + V\, dp - G\, d\varphi. \tag{3.310}$$

It is easy to see that for a simple system in which $S$, $p$, and $\varphi$ are constant, in the equilibrium state,

$$d(U + pV - \Phi) = 0. \tag{3.311}$$

We introduce the notation

$$\Lambda = U + pV - \Phi, \tag{3.312}$$

or, using (3.13),

$$\Lambda = TS. \tag{3.313}$$

Using this notation, we can write (3.310) in the form

$$d\Lambda = T\, dS + V\, dp - G\, d\varphi. \tag{3.314}$$

Hence, it is obvious that

$$\left(\frac{\partial \Lambda}{\partial S}\right)_{p,\, \varphi} = -T, \tag{3.315}$$

$$\left(\frac{\partial \Lambda}{\partial p}\right)_{S,\, \varphi} = V, \tag{3.316}$$

and

$$\left(\frac{\partial \Lambda}{\partial \varphi}\right)_{S,\, p} = -G. \tag{3.317}$$

Thus, $\Lambda$ is a characteristic function if expressed in terms of $S$, $p$, and $\varphi$.

For a complex system the situation is the same: if we transform Eq. (3.145) using (3.4), (3.48), and (3.154a), we find that

$$d(U + pV + \xi W - \Phi^*) = T\,dS + V\,dp + W\,d\xi - G\,d\varphi^*. \qquad (3.318)$$

Combining this with (3.59), we see that

$$U + pV + \xi W - \Phi^* = TS \qquad (3.319)$$

and, hence, bearing in mind (3.313), we can write (3.318) in the form

$$d\Lambda = T\,dS + V\,dp + W\,d\xi - G\,d\varphi^*. \qquad (3.320)$$

It is clear that for a complex system in which $S$, $p$, $\xi$, and $\varphi^*$ are constant, in the equilibrium state,

$$d\Lambda = 0. \qquad (3.321)$$

From (3.320) it is obvious that

$$\left(\frac{\partial \Lambda}{\partial S}\right)_{p,\,\xi,\,\varphi^*} = T, \qquad (3.322)$$

$$\left(\frac{\partial \Lambda}{\partial p}\right)_{S,\,\xi,\,\varphi^*} = V, \qquad (3.323)$$

$$\left(\frac{\partial \Lambda}{\partial \xi}\right)_{S,\,p,\,\varphi^*} = W, \qquad (3.324)$$

and

$$\left(\frac{\partial \Lambda}{\partial \varphi^*}\right)_{S,\,p,\,\xi} = -G. \qquad (3.325)$$

It is interesting to note that the characteristic function $\Lambda$ is not a thermodynamic potential. Indeed, if we substitute in Eq. (3.145) the quantity $\xi\,dW$ using (1.7), we can write (3.145) in the following form:

$$T\,dS = dU + p\,dV - dL^* - \varphi^*\,dG. \qquad (3.326)$$

Using Legendre transformations (3.4) and (3.154a), we obtain

$$d(U + pV - \Phi^*) = T\,dS + V\,dp - G\,d\varphi^* - dL^*. \qquad (3.327)$$

Hence it is clear that for a complex thermodynamic system in which $S$, $p$, and $\varphi^*$ are constant

$$dL^* = -\,d(U + pV - \Phi^*). \qquad (3.328)$$

But from (3.59) it is obvious that

$$U + pV - \Phi^* = TS - \xi W, \qquad (3.329)$$

or, using (3.313),

$$U + pV - \Phi^* = \Lambda - \xi W. \qquad (3.330)$$

If we combine this relation with Eq. (3.328), we find that

$$dL^* = -d\Lambda + d(\xi W). \tag{3.331}$$

Hence it is clear that under the given conditions of interaction with the surroundings, the work $L^*$ performed by a complex system is not done at the expense of the characteristic function $\Lambda$. Therefore, the function $\Lambda$ does not have the properties of a thermodynamic potential. As seen from (3.331), the function $\Lambda - \xi W = TS - \xi W$ is a thermodynamic potential for this system; it is also a characteristic function.

This can easily be shown in the following way. If to transform Eq. (3.145) we use only (3.4) and (3.154a) and we do not substitute $\xi W$ by means of (3.48), instead of (3.318) we have

$$d(U + pV - \Phi^*) = T\,dS + V\,dp - \xi\,dW - G\,d\varphi^*, \tag{3.332}$$

or, using (3.329),

$$d(TS - \xi W) = T\,dS + V\,dp - \xi\,dW - G\,d\varphi^*. \tag{3.333}$$

Whence, it is clear that for a system in which $S$, $p$, $W$, and $\varphi^*$ are constant,[6] in the equilibrium state,

$$d(TS - \xi W) = 0. \tag{3.334}$$

If we introduce the notation

$$\Xi = TS - \xi W, \tag{3.335}$$

we can write (3.333) in the form

$$d\Xi = T\,dS + V\,dp - \xi\,dW - G\,d\varphi^*. \tag{3.336}$$

From this it follows that

$$\left(\frac{\partial \Xi}{\partial S}\right)_{p,\,W,\,\varphi^*} = T, \tag{3.337}$$

$$\left(\frac{\partial \Xi}{\partial p}\right)_{S,\,W,\,\varphi^*} = V, \tag{3.338}$$

$$\left(\frac{\partial \Xi}{\partial W}\right)_{S,\,p,\,\varphi^*} = -\xi, \tag{3.339}$$

and

$$\left(\frac{\partial \Xi}{\partial \varphi^*}\right)_{S,\,p,\,W} = -G. \tag{3.340}$$

The above relations show that the function $\Xi$ is indeed a characteristic function if expressed in terms of $S$, $p$, $W$, and $\varphi^*$. Obviously,

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[6] The peculiarity of these conditions of interaction between the system and its surroundings consists in that along with the conditions that $S$ and $\varphi^*$ be kept constant, in relation to one type of work (the work of expansion), the value of the generalized force, pressure $p$, remains constant, while in relation to another type of work the value of the generalized coordinate $W$ remains constant.

if we substitute $\xi\, dW$ using (1.7) and (3.329) in Eq. (3.336), we can transform the latter equation to

$$d\Xi = T\,dS + V\,dp - G\,d\varphi^* - dL^*. \tag{3.341}$$

It is clear that for a thermodynamic system in which $S$, $p$, and $\varphi^*$ are constant, in the equilibrium state,

$$dL^* = -\,d\Xi, \tag{3.342}$$

i.e. the system can perform work, $L^*$, at the expense of the characteristic function $\Xi$. Consequently, the function $\Xi$ is a thermodynamic potential. Naturally, (3.342) is equivalent to (3.331).

3.5.3. Let us now consider Eq. (3.144) written in the form (3.266):

$$dS = \frac{1}{T}\,dU + \frac{p}{T}\,dV - \frac{\varphi}{T}\,dG.$$

If we use the Legendre transformation (3.267)

$$\frac{\varphi}{T}\,dG = d\left(\frac{\varphi G}{T}\right) - Gd\left(\frac{\varphi}{T}\right)$$

and Eq. (3.42), we can write Eq. (3.266) in the following form:

$$dS = \frac{1}{T}\,dU + \frac{p}{T}\,dV + Gd\left(\frac{\varphi}{T}\right) - d\left(\frac{\Phi}{T},\right) \tag{3.343}$$

or, using (3.197),

$$dS = \frac{1}{T}\,dU + \frac{p}{T}\,dV - G\,d\tilde{\varphi} - d\left(\frac{\Phi}{T}\right). \tag{3.344}$$

This equation can be transformed with the help of (3.165)

$$\frac{1}{T}\,dU = d\left(\frac{U}{T}\right) - Ud\left(\frac{1}{T}\right)$$

and (3.172)

$$\frac{p}{T}\,dV = d\left(\frac{pV}{T}\right) - Vd\left(\frac{p}{T}\right).$$

There are four ways in which we can transform Eq. (3.343): using both (3.165) and (3.172), using only (3.165), using only (3.172), and using neither (3.165) nor (3.172).

It is easy to show that the first case results in the Gibbs-Duhem equation in the form (3.344).

The second yields Eq. (3.268), which we already know (on the basis of the equation that introduced the Kramers function (3.270)).

If we consider the two remaining cases, we obtain interesting results.

(1) Substituting in (3.343) the quantity $(p/T)\,dV$ by means of the Legendre transformation (3.172), we obtain

$$d\left(S-\frac{pV}{T}+\frac{\Phi}{T}\right)=\frac{1}{T}\,dU-V\,d\left(\frac{p}{T}\right)+G\,d\left(\frac{\varphi}{T}\right). \tag{3.345}$$

We see that for a simple system in which $U$, $p/T$, and $\varphi/T$ are constant, in the equilibrium state,

$$d\left(S-\frac{pV}{T}+\frac{\Phi}{T}\right)=0. \tag{3.346}$$

Taking into account (3.13), we see that

$$S-\frac{pV}{T}+\frac{\Phi}{T}=\frac{U}{T}. \tag{3.347}$$

We introduce the notation

$$\tilde{U}=S-\frac{pV}{T}+\frac{\Phi}{T}. \tag{3.348}$$

From (3.347) if follows that

$$\tilde{U}=U/T. \tag{3.349}$$

Let us now write (3.345) in the form

$$d\tilde{U}=\frac{1}{T}\,dU-V\,d\left(\frac{p}{T}\right)+G\,d\left(\frac{\varphi}{T}\right), \tag{3.350}$$

whence the obvious relations

$$\left(\frac{\partial\tilde{U}}{\partial U}\right)_{p/T,\,\varphi/T}=\frac{1}{T}, \tag{3.351}$$

$$\left(\frac{\partial\tilde{U}}{\partial\frac{p}{T}}\right)_{U,\,\varphi/T}=-V, \tag{3.352}$$

and

$$\left(\frac{\partial\tilde{U}}{\partial\frac{\varphi}{T}}\right)_{U,\,p/T}=G, \tag{3.353}$$

which show that the function $\tilde{U}$ is a characteristic function if expressed in terms of $U$, $p/T$, and $\varphi/T$.

In the same way, for a complex system Eq. (3.277)

$$dS=\frac{1}{T}\,dU+\frac{p}{T}\,dV+\frac{\xi}{T}\,dW-\frac{\varphi^*}{T}\,dG,$$

which we combine with (3.278) and (3.42a) and write as

$$dS=\frac{1}{T}\,dU+\frac{p}{T}\,dV+\frac{\xi}{T}\,dW-d\left(\frac{\Phi^*}{T}\right)+Gd\left(\frac{\varphi^*}{T}\right), \tag{3.354}$$

can be transformed, via (3.172) and (3.215), to

$$d\tilde{U}^*=\frac{1}{T}\,dU-Vd\left(\frac{p}{T}\right)-Wd\left(\frac{\xi}{T}\right)+Gd\left(\frac{\varphi^*}{T}\right). \tag{3.355}$$

Here

$$\tilde{U}^*=S-\frac{pV}{T}-\frac{\xi W}{T}+\frac{\Phi^*}{T}. \tag{3.356}$$

From (3.59) we find that

$$\tilde{U}^*=\tilde{U}. \tag{3.357}$$

We see that for a complex system in which $U$, $p/T$, $\xi/T$, and $\varphi^*/T$ are constant, in the equilibrium state,

$$d\tilde{U}=0. \tag{3.358}$$

From (3.355) it is obvious that

$$\left(\frac{\partial\tilde{U}}{\partial U}\right)_{p/T,\ \xi/T,\ \varphi^*T}=\frac{1}{T}, \tag{3.359}$$

$$\left(\frac{\partial\tilde{U}}{\partial\frac{p}{T}}\right)_{U,\ \xi/T,\ \varphi^*/T}=-V, \tag{3.360}$$

$$\left(\frac{\partial\tilde{U}}{\partial\frac{\xi}{T}}\right)_{U,\ p/T,\ \varphi^*/T}=-W, \tag{3.361}$$

and

$$\left(\frac{\partial\tilde{U}}{\partial\frac{\varphi^*}{T}}\right)_{U,\ p/T,\ \xi/T}=G. \tag{3.362}$$

It is easy to see that the function $\tilde{U}$ does not have the propertieg of a thermodynamic potential. Indeed, if we write (3.215), bearins in mind (1.7), in the form

$$-Wd\left(\frac{\xi}{T}\right)=\frac{1}{T}\,dL^*-d\left(\frac{\xi W}{T}\right), \tag{3.363}$$

then, using this relation, we can transform (3.355) to

$$d\tilde{U}=\frac{1}{T}\,dU-Vd\left(\frac{p}{T}\right)+Gd\left(\frac{\varphi^*}{T}\right)-d\left(\frac{\xi W}{T}\right)+\frac{1}{T}\,dL^*. \tag{3.364}$$

It is clear that for a system in which $U$, $p/T$, and $\varphi^*/T$ are constant,

$$dL^* = T\left[d\tilde{U} + d\left(\frac{\xi W}{T}\right)\right], \tag{3.365}$$

or, in accordance with (3.349),

$$dL^* = Td\,\frac{U+\xi W}{T}. \tag{3.366}$$

Therefore, the work $L^*$ is not done at the expense of the characteristic function $\tilde{U}$; hence, $\tilde{U}$ is not a thermodynamic potential.

(2) Let us now consider Eq. (3.343) without applying Legendre transformations (3.165) and (3.172). Equation (3.343) can be written thus:

$$d\left(S+\frac{\Phi}{T}\right) = \frac{1}{T}\,dU + \frac{p}{T}\,dV + Gd\left(\frac{\varphi}{T}\right). \tag{3.367}$$

We see that for a simple system in which $U$, $V$, and $\varphi/T$ are constant, in the equilibrium state,

$$d\,(S + \Phi/T) = 0. \tag{3.368}$$

From (3.15) it follows that

$$S + \Phi/T = H/T. \tag{3.369}$$

Let us introduce the notation

$$\tilde{H} = S + \Phi/T. \tag{3.370}$$

Obviously,

$$\tilde{H} = H/T. \tag{3.371}$$

Using this notation, we can write (3.367) in the form

$$d\tilde{H} = \frac{1}{T}\,dU + \frac{p}{T}\,dV + Gd\left(\frac{\varphi}{T}\right), \tag{3.372}$$

whence

$$\left(\frac{\partial \tilde{H}}{\partial U}\right)_{V,\,\varphi/T} = \frac{1}{T}, \tag{3.373}$$

$$\left(\frac{\partial \tilde{H}}{\partial V}\right)_{U,\,\varphi/T} = \frac{p}{T}, \tag{3.374}$$

and

$$\left(\frac{\partial \tilde{H}}{\partial \frac{\varphi}{T}}\right)_{U,\,V} = G. \tag{3.375}$$

From these relations it follows that $\tilde{H}$ is a characteristic function if expressed in terms of $U$, $V$, and $\varphi/T$.

For a complex system we can write Eq. (3.354) in the following way:

$$d\tilde{H}^* = \frac{1}{T}\,dU + \frac{p}{T}\,dV + \frac{\xi}{T}\,dW + G\,d\left(\frac{\varphi^*}{T}\right), \qquad (3.376)$$

where

$$\tilde{H}^* = S + \Phi^*/T. \qquad (3.377)$$

Using (3.60), we find that

$$\tilde{H}^* = H^*/T. \qquad (3.378)$$

From (3.376) it follows that for a complex system in which $U$, $V$, $W$, and $\varphi^*/T$ are constant, in the equilibrium state,

$$d\tilde{H}^* = 0. \qquad (3.379)$$

From (3.376) it also follows that

$$\left(\frac{\partial \tilde{H}^*}{\partial U}\right)_{V,\,W,\,\varphi^*/T} = \frac{1}{T}, \qquad (3.380)$$

$$\left(\frac{\partial \tilde{H}^*}{\partial V}\right)_{U,\,W,\,\varphi^*/T} = \frac{p}{T}, \qquad (3.381)$$

$$\left(\frac{\partial \tilde{H}^*}{\partial W}\right)_{U,\,V,\,\varphi^*/T} = \frac{\xi}{T}, \qquad (3.382)$$

and

$$\left(\frac{\partial H^*}{\partial \dfrac{\varphi^*}{T}}\right)_{U,\,V,\,W} = G. \qquad (3.383)$$

Hence, the function $\tilde{H}^*$ is a characteristic function if expressed in terms of $U$, $V$, $W$, and $\varphi^*/T$.

Next, using (1.7), we can write Eq. (3.376) in the form

$$d\tilde{H}^* = \frac{1}{T}\,dU + \frac{p}{T}\,dV + G\,d\left(\frac{\varphi^*}{T}\right) + \frac{1}{T}\,dL^*. \qquad (3.384)$$

We see that for a system in which $U$, $V$, and $\varphi^*/T$ are constant,

$$dL^* = T\,d\tilde{H}^*, \qquad (3.385)$$

i.e. the work $L^*$ is not done at the expense of the characteristic function $\tilde{H}^*$ and, hence, $\tilde{H}^*$ is not a thermodynamic potential.

The characteristic functions discussed in this section are interesting, first of all, from the pedagogical point of view, since they constitute the group of characteristic functions for thermodynamic systems with variable amount of substance.

3.5.4. In conclusion let us consider one more problem. We have shown above that if we substitute in Eq. (3.144) the quantities $T\,dS$, $p\,dV$, $\xi\,dW$, and $\varphi^*\,dG$ using Legendre transformations (3.7), (3.4), (3.48), and (3.154a), we obtain the Gibbs-Duhem equation for complex systems (3.158). Similarly, if we substitute in Eq. (3.277) the quantities $(1/T)\,dU$, $(p/T)\,dV$, $(\xi/T)\,dW$, and $(\varphi^*/T)\,dG$ using Legendre transformations (3.165), (3.172), (3.215), and (3.304), we obtain the Gibbs-Duhem equation for complex systems (3.244). These Gibbs-Duhem equations show that for the group of variables $T$, $p$, $\xi$ and $\varphi^*$ and, likewise, for the group of variables $1/T$, $p/T$, $\xi/T$, and $\varphi^*/T$ there are no characteristic functions. However, it is interesting to discuss what amount of work $L^*$ can be performed by a complex system under the following conditions of interaction with the surroundings: $T$, $p$, and $\varphi^*$ are constant; and $1/T$, $p/T$, and $\varphi^*/T$ are constant.

If we use (1.7) and write Eq. (3.145) in the form

$$T\,dS = dU + p\,dV - \varphi^*\,dG + dL^*, \tag{3.386}$$

then using Legendre transformations (3.4), (3.7), and (3.154a), we can write this equation in the following form:

$$d\,(TS - U - pV + \Phi^*) = S\,dT - V\,dp + G\,d\varphi^* + dL^*, \tag{3.387}$$

or, with due regard for (3.59),

$$d\,(\xi W) = S\,dT - V\,dp + G\,d\varphi^* + dL^*. \tag{3.388}$$

Hence, we see that for a complex system in which $T$, $p$, and $\varphi^*$ are constant,

$$dL^* = d\,(\xi W). \tag{3.389}$$

Similarly, if we take into account (1.7) and write (3.277) in the form

$$dS = \frac{1}{T}\,dU + \frac{p}{T}\,dV - \frac{\varphi^*}{T}\,dG + \frac{1}{T}\,dL^*. \tag{3.390}$$

using Legendre transformations (3.165), (3.172), and (3.278), we can reduce (3.390) to

$$d\left(S - \frac{U}{T} - \frac{pV}{T} + \frac{\Phi^*}{T}\right) = -U d\left(\frac{1}{T}\right) - V d\left(\frac{p}{T}\right) + G d\left(\frac{\varphi^*}{T}\right) + \frac{1}{T}\,dL^* \tag{3.391}$$

or, with due regard for (3.59),

$$d\left(\frac{\xi W}{T}\right) = -U d\left(\frac{1}{T}\right) - V d\left(\frac{p}{T}\right) + G d\left(\frac{\varphi^*}{T}\right) + \frac{1}{T}\,dL^*. \tag{3.392}$$

Therefore, for a complex system in which $1/T$, $p/T$, and $\varphi^*/T$ are constant,

$$dL^* = Td\left(\frac{\xi W}{T}\right) \tag{3.393}$$

or, since $T$ is constant,

$$dL^* = d(\xi W), \tag{3.394}$$

which coincides with (3.389). This is obvious *a priori*, since the conditions of interaction of the two systems with the surroundings are the same.

Table 3.1 gives the characteristic functions discussed in this chapter.

TABLE 3.1

| Simple systems | | Complex systems | |
|---|---|---|---|
| Variables | Characteristic function | Variables | Characteristic function |
| Constant amount of substance | | | |
| $S, V$ | $U$ | $S, V, W$ | $U$ |
| $S, p$ | $H = U + pV$ | $S, p, \xi$ | $H^* = U + pV + \xi W$ |
| $T, V$ | $F = U - TS$ | $T, V, W$ | $F = U - TS$ |
| $T, p$ | $\Phi = U + pV - TS$ | $T, p, \xi$ | $\varphi^* = U + pV + \xi W - TS$ |
| $U, V$ | $S$ | $U, V, W$ | $S$ |
| $U, p/T$ | $I = (TS - pV)/T$ | $U, p/T, \xi/T$ | $I^* = (TS - pV - \xi W)/T$ |
| $1/T, V$ | $\tilde{F} = -F/T$ | $1/T, V, W$ | $\tilde{F} = -F/T$ |
| $1/T, p/T$ | $\tilde{\Phi} = -\Phi/T$ | $1/T, p/T, \xi/T$ | $\tilde{\Phi} = -\Phi^*/T$ |
| Variable amount of substance | | | |
| $S, V, \varphi$ | $\Pi = TS - pV$ | $S, V, W, \varphi^*$ | $\Pi^* = TS - pV - \xi W$ |
| $S, p, \varphi$ | $\Lambda = TS$ | $S, p, \xi, \varphi^*$ | $\Lambda = TS$ |
| $T, V, \varphi$ | $\Gamma = -pV$ | $T, V, W, \varphi^*$ | $\Gamma^* = -pV - \xi W$ |
| $T, p, \varphi$ | | $T, p, \xi, \varphi^*$ | |
| $U, V, \varphi/T$ | $\tilde{H} = H/T$ | $U, V, W, \varphi^*/T$ | $\tilde{H}^* = H^*/T$ |
| $U, p/T, \varphi/T$ | $\tilde{U} = U/T$ | $U, p/T, \xi/T, \varphi^*/T$ | $\tilde{U} = U/T$ |
| $1/T, V, \varphi/T$ | $\tilde{\Gamma} = -\Gamma/T$ | $1/T, V, W, \varphi^*/T$ | $\tilde{\Gamma}^* = -\Gamma^*/T$ |
| $1/T, p/T, \varphi/T$ | | $1/T, p/T, \xi/T, \varphi^*/T$ | |

TABLE 3.2

| Interaction between complex thermodynamic system and surroundings | | | Characteristic function | Work of system in equilibrium |
|---|---|---|---|---|
| | | Constant amount of substance | | |
| $S=\text{const}$, | $V=\text{const}$ | | $U$ | $dL^*=-dU$ |
| $S=\text{const}$, | $p=\text{const}$ | | $H$ | $dL^*=-dH$ |
| $T=\text{const}$, | $V=\text{const}$ | | $F$ | $dL^*=-dF$ |
| $T=\text{const}$, | $p=\text{const}$ | | $\Phi$ | $dL^*=-d\Phi$ |
| $U=\text{const}$, | $V=\text{const}$ | | $S$ | $dL^*=T\,dS$ |
| $U=\text{const}$, | $p/T=\text{const}$ | | $I$ | $dL^*=T\,dI$ |
| $1/T=\text{const}$, | $V=\text{const}$ | | $\tilde{F}$ | $dL^*=-dF$ |
| $1/T=\text{const}$, | $p/T=\text{const}$ | | $\tilde{\Phi}$ | $dL^*=-d\Phi$ |
| | | Variable amount of substance | | |
| $S=\text{const}$, | $V=\text{const}$, | $\varphi^*=\text{const}$ | $\Pi$ | $dL^*=-d\Pi^*$ |
| $S=\text{const}$, | $p=\text{const}$, | $\varphi^*=\text{const}$ | $\Lambda$ | $dL^*=-d\,(TS-\xi W)$ |
| $T=\text{const}$, | $V=\text{const}$, | $\varphi^*=\text{const}$ | $\Gamma$ | $dL^*=-d\Gamma^*$ |
| $T=\text{const}$, | $p=\text{const}$, | $\varphi^*=\text{const}$ | | $dL^*=d\,(\xi W)$ |
| $U=\text{const}$, | $V=\text{const}$, | $\varphi^*/T=\text{const}$ | $\tilde{H}$ | $dL^*=T\,dH^*$ |
| $U=\text{const}$, | $p/T=\text{const}$, | $\varphi^*/T=\text{const}$ | $\tilde{U}$ | $dL^*=T\,d\,(U+\xi W)/T$ |
| $1/T=\text{const}$, | $V=\text{const}$, | $\varphi^*/T=\text{const}$ | $\tilde{\Gamma}$ | $dL^*=-d\Gamma^*$ |
| $1/T=\text{const}$, | $p/T=\text{const}$, | $\varphi^*/T=\text{const}$ | | $dL^*=d\,(\xi W)$ |

The relations defining the work $L^*$ that a specific system can perform in the equilibrium state are presented in Table 3.2. These are given for different conditions of interaction between the complex thermodynamic system and its surroundings. We recall that if the work $L^*$ is done at the expense of a characteristic function $N$ (i.e. $dL^*=-dN$), this function is a thermodynamic potential; otherwise it is not.

# 4 The Maxwell Equations

## 4.1 Simple Systems

4.1.1. The most important tools of thermodynamics are the equations derived by J. C. Maxwell. In what follows we will widely use these equations.

The Maxwell equations can be obtained in the following way. The reader will recall (see Chap. 2) that if a differential of a function $z = f(x, y)$ is written in form (2.63)

$$dz = M\,dx + N\,dy$$

and it is known that the differential of this function is total, the relation (2.30) holds:

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y.$$

(1) If we compare Eq. (3.25a)

$$du = T\,ds - p\,dv$$

with (2.63), we find that $M = T$, $N = -p$, $x = s$, and $y = v$. Hence, from (2.30) we obtain

$$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial p}{\partial s}\right)_v. \tag{4.1}$$

(2) If we compare Eq. (3.28a)

$$dh = T\,ds + v\,dp$$

with (2.63), we see that $M = T$, $N = v$, $x = s$, and $y = p$. With this in mind, from (2.30) we find that

$$\left(\frac{\partial T}{\partial p}\right)_s = \left(\frac{\partial v}{\partial s}\right)_p. \tag{4.2}$$

(3) If we compare (3.31a)

$$df = -p\,dv - s\,dT$$

with (2.63), we find that $M = -p$, $N = -s$, $x = v$, and $y = T$. Hence, from (2.30) we obtain

$$\left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T. \tag{4.3}$$

(4) Finally, if we compare (3.34a)

$$d\varphi = v\,dp - s\,dT$$

with (2.63), we find that $M = v$, $N = -s$, $x = p$, and $y = T$. From (2.30) it follows that

$$\left(\frac{\partial v}{\partial T}\right)_p = -\left(\frac{\partial s}{\partial p}\right)_T. \tag{4.4}$$

Relations (4.1)-(4.4) are called the Maxwell equations.

4.1.2. From (2.1) it is obvious that Eqs. (4.1) through (4.4) may be written in "inverted" form:

$$\left(\frac{\partial v}{\partial T}\right)_s = -\left(\frac{\partial s}{\partial p}\right)_v, \tag{4.1a}$$

$$\left(\frac{\partial p}{\partial T}\right)_s = \left(\frac{\partial s}{\partial v}\right)_p, \tag{4.2a}$$

$$\left(\frac{\partial T}{\partial p}\right)_v = \left(\frac{\partial v}{\partial s}\right)_T, \tag{4.3a}$$

and

$$\left(\frac{\partial T}{\partial v}\right)_p = -\left(\frac{\partial p}{\partial s}\right)_T. \tag{4.4a}$$

4.1.3. Equations (4.1) through (4.4a) are written for the specific (per unit mass) values, $v$ and $s$, but the same can be derived for the total quantities, $V$ and $S$, relating to the entire thermodynamic system:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V, \tag{4.1b}$$

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p, \tag{4.2b}$$

$$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T, \tag{4.3b}$$

$$\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T; \tag{4.4b}$$

the inverse relations will also have this form.

4.1.4. From what we have said it follows that the Maxwell equations can be considered a particular case of the general relation (2.30) given for thermodynamic quantities.

4.1.5 Naturally, we may ask what relation we will obtain if, together with Eqs. (3.25a), (3.28a), (3.31a), and (3.34a), we consider Eq. (1.27a). Let us write this equation in the form

$$ds = \frac{1}{T}\,du + \frac{p}{T}\,dv \tag{4.5}$$

and compare it with (2.63). We find that $M = 1/T$, $N = p/T$, $x = u$, and $y = v$. Substituting these values into (2.30), we get

$$\left(\frac{\partial T}{\partial v}\right)_u = T\left(\frac{\partial p}{\partial u}\right)_v - p\left(\frac{\partial T}{\partial u}\right)_v. \tag{4.6}$$

Since in accordance with (2.67)

$$\left(\frac{\partial T}{\partial v}\right)_u = -\left(\frac{\partial T}{\partial u}\right)_v\left(\frac{\partial u}{\partial v}\right)_T \tag{4.7}$$

and in accordance with (2.6)

$$\left(\frac{\partial p}{\partial u}\right)_v = \left(\frac{\partial p}{\partial T}\right)_v\left(\frac{\partial T}{\partial u}\right)_v, \tag{4.8}$$

we obtain from (4.7)

$$\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v - p. \tag{4.9}$$

This relation gives the variation in the internal energy with the specific volume on an isotherm. It is used in various thermodynamic calculations, but the Maxwell equations are far more significant and universal; moreover, relation (4.9) may be easily derived from one of the Maxwell equations (see Sec. 5.1).

4.1.6. Sometimes the following method of deriving the Maxwell equations is given. Let us denote by $x$ and $y$ two variables that imply any pair from the four quantities $p$, $v$, $T$, and $s$. From Eq. (3.25a)

$$du = T\,ds - p\,dv$$

it follows that

$$\left(\frac{\partial u}{\partial x}\right)_y = T\left(\frac{\partial s}{\partial x}\right)_y - p\left(\frac{\partial v}{\partial x}\right)_v \tag{4.10}$$

and

$$\left(\frac{\partial u}{\partial y}\right)_x = T\left(\frac{\partial s}{\partial y}\right)_x - p\left(\frac{\partial v}{\partial y}\right)_x. \tag{4.11}$$

Differentiating the first of these relations with respect to $y$ with $x$ constant, and the second with respect to $x$ with $y$ constant, we obtain, respectively,

$$\frac{\partial^2 u}{\partial x\,\partial y} = \left(\frac{\partial T}{\partial y}\right)_x\left(\frac{\partial s}{\partial x}\right)_y + T\frac{\partial^2 s}{\partial x\,\partial y} - \left(\frac{\partial p}{\partial y}\right)_x\left(\frac{\partial v}{\partial x}\right)_y - p\frac{\partial^2 v}{\partial x\,\partial y} \tag{4.12}$$

and

$$\frac{\partial^2 u}{\partial y\,\partial x} = \left(\frac{\partial T}{\partial x}\right)_y\left(\frac{\partial s}{\partial y}\right)_x + T\frac{\partial^2 s}{\partial y\,\partial x} - \left(\frac{\partial p}{\partial x}\right)_y\left(\frac{\partial v}{\partial y}\right)_x - p\frac{\partial^2 v}{\partial y\,\partial x}. \tag{4.13}$$

Equating the right-hand sides of these relations we obtain

$$\left(\frac{\partial T}{\partial y}\right)_x\left(\frac{\partial s}{\partial x}\right)_y-\left(\frac{\partial p}{\partial y}\right)_x\left(\frac{\partial v}{\partial x}\right)_y=\left(\frac{\partial T}{\partial x}\right)_y\left(\frac{\partial s}{\partial y}\right)_x-\left(\frac{\partial p}{\partial x}\right)_y\left(\frac{\partial v}{\partial y}\right)_x. \tag{4.14}$$

If we substitute $p$, $v$, $T$, and $s$ for $x$ and $y$, we see that four variants of such a substitution are possible:

(1) $x = v$, $y = s$; (3) $x = v$, $y = T$;
(2) $x = p$, $y = s$; (4) $x = p$, $y = T$

(since Eq. (4.14) is symmetric with respect to $x$ and $y$, substituting $x = v$, $y = s$ for $x = s$, $y = v$, and so on does not yield a new result).

Substituting $x = v$ and $y = s$ into (4.14), we obtain

$$\left(\frac{\partial T}{\partial s}\right)_v\left(\frac{\partial s}{\partial v}\right)_s-\left(\frac{\partial p}{\partial s}\right)_v\left(\frac{\partial v}{\partial v}\right)_s=\left(\frac{\partial T}{\partial v}\right)_s\left(\frac{\partial s}{\partial s}\right)_v-\left(\frac{\partial p}{\partial v}\right)_s\left(\frac{\partial v}{\partial s}\right)_v. \tag{4.15}$$

Since, obviously, $(\partial s/\partial v)_s = 0$ and $(\partial v/\partial s)_v = 0$ but $(\partial v/\partial v)_s = 1$ and $(\partial s/\partial s)_v = 1$, from (4.15) it follows that

$$\left(\frac{\partial p}{\partial s}\right)_v=-\left(\frac{\partial T}{\partial v}\right)_s,$$

which is the Maxwell equation (4.1).

Similarly, the second, third, and fourth variants of the substitution yield, respectively, the Maxwell equations (4.2), (4.3), and (4.4).

This method of deriving the Maxwell equations is, perhaps, more elegant than the one considered in Sec. 4.1.1, but the latter is clearer.

## 4.2 Complex Systems

4.2.1. If a thermodynamic system performs work other than work of expansion, the Maxwell equations are formulated in the following way.

(1) From the combined equation of the first and second laws of thermodynamics for such systems, (1.30a), it follows that (see Eq. (3.62a))

$$du = T\,ds - p\,dv - \xi\,dw.$$

We note that $\xi$ is a generalized force (save for pressure $p$) and $w$ is a generalized coordinate (save for specific volume $v$).

For the case with $v$ constant we obtain

$$du = T\,ds - \xi\,dw. \tag{4.16}$$

With the aid of the method discussed in Sec. 4.1.1 and Eq. (2.30) we find that

$$\left(\frac{\partial T}{\partial w}\right)_{s,\ v}=-\left(\frac{\partial \xi}{\partial s}\right)_{w,\ v}. \tag{4.17}$$

Similarly, for the case with $w$ constant we find from (3.62a) and (2.30) that

$$\left(\frac{\partial T}{\partial v}\right)_{s,\ w}=-\left(\frac{\partial p}{\partial s}\right)_{v,\ w}. \tag{4.18}$$

(2) Equation (3.66a)

$$dh^* = T\,ds + vdp + wd\xi,$$

where $h^*$ is the enthalpy of a complex system defined by relation (1.15a)

$$h^* = u + pv + \xi w,$$

for the case with $p$ constant can be written thus:

$$dh^* = T\,ds + wd\xi. \tag{4.19}$$

In accordance with (2.30) we find from this relation that

$$\left(\frac{\partial T}{\partial \xi}\right)_{s,\ p}=\left(\frac{\partial w}{\partial s}\right)_{\xi,\ p}. \tag{4.20}$$

Similarly, for the case with $\xi$ constant we find from (3.66a) and (2.30) that

$$\left(\frac{\partial T}{\partial p}\right)_{s,\ \xi}=\left(\frac{\partial v}{\partial s}\right)_{p,\ \xi}. \tag{4.21}$$

(3) Equation (3.70a)

$$df = -\,pdv - \xi dw - sdT,$$

where $f$ is the free energy of a complex system defined by the general relation (3.41), for the case with $v$ constant is

$$df = -\,\xi dw - sdT. \tag{4.22}$$

In accordance with (2.30) we find from (4.22) that

$$\left(\frac{\partial \xi}{\partial T}\right)_{w,\ v}=\left(\frac{\partial s}{\partial w}\right)_{T,\ v}. \tag{4.23}$$

Similarly, for the case with $w$ constant we find from (3.70a) and (2.30) that

$$\left(\frac{\partial p}{\partial T}\right)_{v,\ w}=\left(\frac{\partial s}{\partial v}\right)_{T,\ w}. \tag{4.24}$$

(4) Finally, Eq. (3.74a)

$$d\varphi^* = vdp + wd\xi - sdT$$

for the case with $p$ constant is written thus:

$$d\varphi^* = wd\xi - sdT. \tag{4.25}$$

Hence, in accordance with (2.30), we have

$$\left(\frac{\partial w}{\partial T}\right)_{\xi,\ p} = -\left(\frac{\partial s}{\partial \xi}\right)_{T,\ p}. \tag{4.26}$$

Similarly, for the case with $\xi$ constant we find from (3.74a) and (2.30) that

$$\left(\frac{\partial v}{\partial T}\right)_{p,\ \xi} = -\left(\frac{\partial s}{\partial p}\right)_{T,\ \xi}. \tag{4.27}$$

These are the Maxwell equations for complex systems. We see that Eqs. (4.18), (4.21), (4.24), and (4.27) are similar to Eqs. (4.1) through (4.4), the only difference being that the partial derivatives in (4.18) and (4.24) are calculated with $w$ kept constant, and those in (4.21) and (4.27) with $\xi$ constant.

4.2.2. Naturally, the Maxwell equations can also be written in an inverted form:

$$\left(\frac{\partial w}{\partial T}\right)_{s,\ v} = -\left(\frac{\partial s}{\partial \xi}\right)_{w,\ v}, \tag{4.17a}$$

$$\left(\frac{\partial v}{\partial T}\right)_{s,\ w} = -\left(\frac{\partial s}{\partial p}\right)_{v,\ w}, \tag{4.18a}$$

$$\left(\frac{\partial \xi}{\partial T}\right)_{s,\ p} = \left(\frac{\partial s}{\partial w}\right)_{\xi,\ p}, \tag{4.20a}$$

$$\left(\frac{\partial p}{\partial T}\right)_{s,\ \xi} = \left(\frac{\partial s}{\partial v}\right)_{p,\ \xi}, \tag{4.21a}$$

$$\left(\frac{\partial T}{\partial \xi}\right)_{w,\ v} = \left(\frac{\partial w}{\partial s}\right)_{T,\ v}, \tag{4.23a}$$

$$\left(\frac{\partial T}{\partial p}\right)_{v,\ w} = \left(\frac{\partial v}{\partial s}\right)_{T,\ w}, \tag{4.24a}$$

$$\left(\frac{\partial T}{\partial w}\right)_{\xi,\ p} = -\left(\frac{\partial \xi}{\partial s}\right)_{T,\ p}, \tag{4.26a}$$

$$\left(\frac{\partial T}{\partial v}\right)_{p,\ \xi} = -\left(\frac{\partial p}{\partial s}\right)_{T,\ \xi}. \tag{4.27a}$$

4.2.3. The Maxwell equations for complex systems obtained in this section, just as Eqs. (4.1b) through (4.4b), can be written for the total values of $V$, $W$, and $S$ which refer to the entire thermodynamic system:

$$\left(\frac{\partial T}{\partial W}\right)_{S,\,V} = -\left(\frac{\partial \xi}{\partial S}\right)_{W,\,V}, \tag{4.17b}$$

$$\left(\frac{\partial T}{\partial V}\right)_{S,\,W} = -\left(\frac{\partial p}{\partial S}\right)_{V,\,W}, \tag{4.18b}$$

$$\left(\frac{\partial T}{\partial \xi}\right)_{S,\,p} = \left(\frac{\partial W}{\partial S}\right)_{\xi,\,p}, \tag{4.20b}$$

$$\left(\frac{\partial T}{\partial p}\right)_{S,\,\xi} = \left(\frac{\partial V}{\partial S}\right)_{p,\,\xi}, \tag{4.21b}$$

$$\left(\frac{\partial \xi}{\partial T}\right)_{W,\,V} = \left(\frac{\partial S}{\partial W}\right)_{T,\,V}, \tag{4.23b}$$

$$\left(\frac{\partial p}{\partial T}\right)_{V,\,W} = \left(\frac{\partial S}{\partial V}\right)_{T,\,W}, \tag{4.24b}$$

$$\left(\frac{\partial W}{\partial T}\right)_{\xi,\,p} = -\left(\frac{\partial S}{\partial \xi}\right)_{T,\,p}, \tag{4.26b}$$

$$\left(\frac{\partial V}{\partial T}\right)_{p,\,\xi} = -\left(\frac{\partial S}{\partial p}\right)_{T,\,\xi} \tag{4.27b}$$

and, similarly,

$$\left(\frac{\partial W}{\partial T}\right)_{S,\,V} = -\left(\frac{\partial S}{\partial \xi}\right)_{W,\,V}, \tag{4.17c}$$

$$\left(\frac{\partial V}{\partial T}\right)_{S,\,W} = -\left(\frac{\partial S}{\partial p}\right)_{V,\,W}, \tag{4.18c}$$

$$\left(\frac{\partial \xi}{\partial T}\right)_{S,\,p} = \left(\frac{\partial S}{\partial W}\right)_{\xi,\,p}, \tag{4.20c}$$

$$\left(\frac{\partial p}{\partial T}\right)_{S,\,\xi} = \left(\frac{\partial S}{\partial V}\right)_{p,\,\xi}, \tag{4.21c}$$

$$\left(\frac{\partial T}{\partial \xi}\right)_{W,\,V} = \left(\frac{\partial W}{\partial S}\right)_{T,\,V}, \tag{4.23c}$$

$$\left(\frac{\partial T}{\partial p}\right)_{V,\,W} = \left(\frac{\partial V}{\partial S}\right)_{T,\,W}, \tag{4.24c}$$

$$\left(\frac{\partial T}{\partial W}\right)_{\xi,\,p} = -\left(\frac{\partial \xi}{\partial S}\right)_{T,\,p}, \tag{4.26c}$$

$$\left(\frac{\partial T}{\partial V}\right)_{p,\,\xi} = -\left(\frac{\partial p}{\partial S}\right)_{T,\,\xi}. \tag{4.27c}$$

## 4.3 Systems With Variable Amounts of Substance

4.3.1. In Sec. 3.2 we showed that for systems with a variable amount of substance the combined equation of the first and second laws of thermodynamics is written for a simple system in the form (3.144)

$$T\,dS = dU + p\,dV - \varphi\,dG,$$

and for a complex system in the form (3.145)

$$T\,dS = dU + p dV + \xi dW - \varphi^* dG.$$

By the same methods that we applied in Secs. 4.1 and 4.2 to Eqs. (1.27a) and (1.30a), from Eqs. (3.144) and (3.145) we can obtain the Maxwell equations for systems with a variable amount of substance.

4.3.2. We write Eq. (3.144) in the form (3.146)

$$dU = T\,dS - p dV + \varphi dG.$$

Combining this relation with (2.30), we see that for $V$ constant

$$\left(\frac{\partial T}{\partial G}\right)_{S,\,V} = \left(\frac{\partial \varphi}{\partial S}\right)_{G,\,V} \tag{4.28}$$

and for $S$ constant

$$\left(\frac{\partial p}{\partial G}\right)_{V,\,S} = -\left(\frac{\partial \varphi}{\partial V}\right)_{G,\,S}. \tag{4.29}$$

If we employ (3.4) to write (3.146) in the form (3.147)

$$dH = T\,dS + V\,dp + \varphi dG,$$

then, combining this with (2.30), we see that for $p$ constant

$$\left(\frac{\partial T}{\partial G}\right)_{S,\,p} = \left(\frac{\partial \varphi}{\partial S}\right)_{G,\,p} \tag{4.30}$$

and for $S$ constant

$$\left(\frac{\partial V}{\partial G}\right)_{p,\,S} = \left(\frac{\partial \varphi}{\partial p}\right)_{G,\,S}. \tag{4.31}$$

Next, (4.28) together with (3.7) yields (3.148)

$$dF = -\,SdT - pdV + \varphi dG,$$

and if we employ (2.30), we obtain for $V$ constant

$$-\left(\frac{\partial S}{\partial G}\right)_{T,\,V} = \left(\frac{\partial \varphi}{\partial T}\right)_{G,\,V} \tag{4.32}$$

and for $T$ constant

$$-\left(\frac{\partial p}{\partial G}\right)_{V,\,T} = \left(\frac{\partial \varphi}{\partial V}\right)_{G,\,T}. \tag{4.33}$$

Finally, if we combine (4.28) with (3.4) and (3.7), we obtain (3.149)

$$d\Phi = -\,SdT + V\,dp + \varphi dG.$$

Hence, for $p$ constant

$$-\left(\frac{\partial S}{\partial G}\right)_{T,\,p} = \left(\frac{\partial \varphi}{\partial T}\right)_{G,\,p} \tag{4.34}$$

and for $T$ constant

$$\left(\frac{\partial V}{\partial G}\right)_{p,\,T}=\left(\frac{\partial \varphi}{\partial p}\right)_{G,\,T}. \tag{4.35}$$

Obviously, Eqs. (4.28) through (4.35) are the Maxwell equations for a simple system with a variable amount of substance.

4.3.3. The derivatives of $\varphi$ on the right-hand sides of the Maxwell equations for simple systems with a variable amount of substance can be calculated in the following way.

(1) Since the derivative $(\partial\varphi/\partial S)_{G,V}$ is calculated with $G$ kept constant, it is clear that

$$\left(\frac{\partial \varphi}{\partial S}\right)_{G,\,V}=\frac{1}{G}\left(\frac{\partial \varphi}{\partial s}\right)_{v}. \tag{4.36}$$

From Eq. (3.43)

$$\varphi = u + pv - Ts$$

we see that

$$\left(\frac{\partial \varphi}{\partial s}\right)_{v}=\left(\frac{\partial u}{\partial s}\right)_{v}+v\left(\frac{\partial p}{\partial s}\right)_{v}-T-s\left(\frac{\partial T}{\partial s}\right)_{v}. \tag{4.37}$$

Since in accordance with (2.6)

$$\left(\frac{\partial p}{\partial s}\right)_{v}=\left(\frac{\partial p}{\partial T}\right)_{v}\left(\frac{\partial T}{\partial s}\right)_{v}$$

and, as we will show in Sec. 5.3.1,

$$\left(\frac{\partial T}{\partial s}\right)_{v}=\frac{T}{c_v}, \tag{4.38}$$

where $c_v$ is the isochoric heat capacity of the substance, combining (3.26a) with (4.37) we obtain

$$\left(\frac{\partial \varphi}{\partial s}\right)_{v}=\frac{T}{c_v}\left[v\left(\frac{\partial p}{\partial T}\right)_{v}-s\right]. \tag{4.39}$$

Employing (4.36) and (4.39), we obtain from (4.28)

$$\left(\frac{\partial T}{\partial G}\right)_{S,\,V}=\frac{T}{Gc_v}\left[v\left(\frac{\partial p}{\partial T}\right)_{v}-s\right]. \tag{4.40}$$

(2) It is also obvious that

$$\left(\frac{\partial \varphi}{\partial V}\right)_{G,\,S}=\frac{1}{G}\left(\frac{\partial \varphi}{\partial v}\right)_{s}. \tag{4.41}$$

From Eq. (3.43) it follows that

$$\left(\frac{\partial \varphi}{\partial v}\right)_{s}=\left(\frac{\partial u}{\partial v}\right)_{s}+p+v\left(\frac{\partial p}{\partial v}\right)_{s}-s\left(\frac{\partial T}{\partial v}\right)_{s}. \tag{4.42}$$

If we take into account (3.27a) and bear in mind that according to (2.6)

$$\left(\frac{\partial T}{\partial v}\right)_s=\left(\frac{\partial T}{\partial p}\right)_s\left(\frac{\partial p}{\partial v}\right)_s, \tag{4.43}$$

we obtain

$$\left(\frac{\partial \varphi}{\partial v}\right)_s=\left(\frac{\partial p}{\partial v}\right)_s\left[v-s\left(\frac{\partial T}{\partial p}\right)_s\right]. \tag{4.44}$$

Combining Eq. (4.29) with (4.44) and (4.41), we have

$$\left(\frac{\partial p}{\partial G}\right)_{V,\,S}=-\frac{1}{G}\left(\frac{\partial p}{\partial v}\right)_s\left[v-s\left(\frac{\partial T}{\partial p}\right)_s\right]. \tag{4.45}$$

(3) We can easily show that

$$\left(\frac{\partial \varphi}{\partial S}\right)_{G,\,p}=\frac{1}{G}\left(\frac{\partial \varphi}{\partial s}\right)_p. \tag{4.46}$$

From Eq. (3.44)

$$\varphi=h-Ts$$

it follows that

$$\left(\frac{\partial \varphi}{\partial s}\right)_p=\left(\frac{\partial h}{\partial s}\right)_p-T-s\left(\frac{\partial T}{\partial s}\right)_p. \tag{4.47}$$

Taking into account (3.29a) and the following relation (see Sec. 5.3.1)

$$\left(\frac{\partial T}{\partial s}\right)_p=\frac{T}{c_p}, \tag{4.48}$$

from (4.47) we obtain

$$\left(\frac{\partial \varphi}{\partial s}\right)_p=-\frac{Ts}{c_p} \tag{4.49}$$

Combining (4.49) and (4.46), from (4.30) we obtain

$$\left(\frac{\partial T}{\partial G}\right)_{S,\,p}=-\frac{Ts}{Gc_p}. \tag{4.50}$$

(4) We can also show

$$\left(\frac{\partial \varphi}{\partial p}\right)_{G,\,S}=\left(\frac{\partial \varphi}{\partial p}\right)_s. \tag{4.51}$$

From (3.44) it follows that

$$\left(\frac{\partial \varphi}{\partial p}\right)_s=\left(\frac{\partial h}{\partial p}\right)_s-s\left(\frac{\partial T}{\partial p}\right)_s, \tag{4.52}$$

or, with due regard for (3.30a),

$$\left(\frac{\partial \varphi}{\partial p}\right)_s=v-s\left(\frac{\partial T}{\partial p}\right)_s. \tag{4.53}$$

Combining this with (4.51), from (4.31) we find that

$$\left(\frac{\partial V}{\partial G}\right)_{p,S}=v-s\left(\frac{\partial T}{\partial p}\right)_s. \tag{4.54}$$

(5) Further, we can prove that

$$\left(\frac{\partial \varphi}{\partial T}\right)_{G,V}=\left(\frac{\partial \varphi}{\partial T}\right)_v. \tag{4.55}$$

By differentiating (3.43), we obtain

$$\left(\frac{\partial \varphi}{\partial T}\right)_v=\left(\frac{\partial u}{\partial T}\right)_v+v\left(\frac{\partial p}{\partial T}\right)_v-T\left(\frac{\partial s}{\partial T}\right)_v-s. \tag{4.56}$$

Since (see Sec. 4.3.1)

$$\left(\frac{\partial u}{\partial T}\right)_v=T\left(\frac{\partial s}{\partial T}\right)_v=c_v, \tag{4.57}$$

we have

$$\left(\frac{\partial \varphi}{\partial T}\right)_v=v\left(\frac{\partial p}{\partial T}\right)_v-s. \tag{4.58}$$

Combining this with (4.55) and (4.32), we have

$$\left(\frac{\partial S}{\partial G}\right)_{T,V}=s-v\left(\frac{\partial p}{\partial T}\right)_v. \tag{4.59}$$

(6) We can easily show that

$$\left(\frac{\partial \varphi}{\partial V}\right)_{G,T}=\frac{1}{G}\left(\frac{\partial \varphi}{\partial v}\right)_T. \tag{4.60}$$

From (3.43) we see that

$$\left(\frac{\partial \varphi}{\partial v}\right)_T=\left(\frac{\partial u}{\partial v}\right)_T+p+v\left(\frac{\partial p}{\partial v}\right)_T-T\left(\frac{\partial s}{\partial v}\right)_T. \tag{4.61}$$

Since (see Sec. 5.1.1)

$$\left(\frac{\partial u}{\partial v}\right)_T=T\left(\frac{\partial p}{\partial T}\right)_v-p, \tag{4.62}$$

in accordance with the Maxwell equation (4.3) from (4.62) we obtain

$$\left(\frac{\partial \varphi}{\partial v}\right)_T=v\left(\frac{\partial p}{\partial v}\right)_T. \tag{4.63}$$

Thus, taking into account (4.60), we can transform Eq. (4.33) to

$$\left(\frac{\partial p}{\partial G}\right)_{V,T}=-\frac{v}{G}\left(\frac{\partial p}{\partial v}\right)_T. \tag{4.64}$$

(7) It is obvious that

$$\left(\frac{\partial \varphi}{\partial T}\right)_{G,p}=\left(\frac{\partial \varphi}{\partial T}\right)_p. \tag{4.65}$$

If we use (4.65) and (3.35a), from (4.34) we obtain

$$\left(\frac{\partial S}{\partial G}\right)_{T,\,p} = -s. \tag{4.66}$$

(8) Finally, we see that

$$\left(\frac{\partial \varphi}{\partial p}\right)_{G,\,T} = \left(\frac{\partial \varphi}{\partial p}\right)_{T}. \tag{4.67}$$

Combining this with (3.36a), from (4.35) we obtain

$$\left(\frac{\partial V}{\partial G}\right)_{p,\,T} = v. \tag{4.68}$$

These relationships define more precisely the Maxwell equations for simple systems with a variable amount of substance.

4.3.4. The Maxwell equations for complex systems with a variable amount of substance can be obtained by a method similar to that used in Sec. 4.3.2.

From Eq. (3.150)

$$dU = T\,dS - p dV - \xi dW + \varphi^* dG$$

it follows that

$$\left(\frac{\partial T}{\partial G}\right)_{S,\,V,\,W} = \left(\frac{\partial \varphi^*}{\partial S}\right)_{G,\,V,\,W}, \tag{4.69}$$

$$\left(\frac{\partial p}{\partial G}\right)_{V,\,W,\,S} = -\left(\frac{\partial \varphi^*}{\partial V}\right)_{G,\,W,\,S}, \tag{4.70}$$

$$\left(\frac{\partial \xi}{\partial G}\right)_{W,\,V,\,S} = -\left(\frac{\partial \varphi^*}{\partial W}\right)_{G,\,V,\,S}. \tag{4.71}$$

From Eq. (3.151)

$$dH^* = T\,dS + V\,dp + W d\xi + \varphi^* dG$$

it follows that

$$\left(\frac{\partial T}{\partial G}\right)_{S,\,p,\,\xi} = \left(\frac{\partial \varphi^*}{\partial S}\right)_{G,\,p,\,\xi}, \tag{4.72}$$

$$\left(\frac{\partial V}{\partial G}\right)_{p,\,\xi,\,S} = \left(\frac{\partial \varphi^*}{\partial p}\right)_{G,\,\xi,\,S}, \tag{4.73}$$

$$\left(\frac{\partial W}{\partial G}\right)_{\xi,\,p,\,S} = \left(\frac{\partial \varphi^*}{\partial \xi}\right)_{G,\,p,\,S}. \tag{4.74}$$

From Eq. (3.152)

$$dF = -S\,dT - p dV - \xi dW + \varphi^* dG$$

it follows that

$$-\left(\frac{\partial S}{\partial G}\right)_{T,\,V,\,W}=\left(\frac{\partial\varphi^*}{\partial T}\right)_{G,\,V,\,W}, \tag{4.75}$$

$$-\left(\frac{\partial p}{\partial G}\right)_{V,\,W,\,T}=\left(\frac{\partial\varphi^*}{\partial V}\right)_{G,\,W,\,T}, \tag{4.76}$$

$$-\left(\frac{\partial \xi}{\partial G}\right)_{W,\,V,\,T}=\left(\frac{\partial\varphi^*}{\partial W}\right)_{G,\,V,\,T}. \tag{4.77}$$

Finally, from (3.153)

$$d\Phi^* = -S\,dT + V\,dp + W{\cdot}d\xi + \varphi^*\,dG$$

it follows that

$$-\left(\frac{\partial S}{\partial G}\right)_{T,\,p,\,\xi}=\left(\frac{\partial\varphi^*}{\partial T}\right)_{G,\,p,\,\xi}, \tag{4.78}$$

$$-\left(\frac{\partial V}{\partial G}\right)_{p,\,\xi,\,T}=\left(\frac{\partial\varphi^*}{\partial p}\right)_{G,\,\xi,\,T}, \tag{4.79}$$

$$\left(\frac{\partial W}{\partial G}\right)_{\xi,\,p,\,T}=\left(\frac{\partial\varphi^*}{\partial \xi}\right)_{G,\,p,\,T}. \tag{4.80}$$

Of course, the derivatives of $\varphi^*$ on the right-hand sides of Eqs. (4.69) through (4.80) can be calculated by using relations similar to the above mentioned equations (4.40), (4.45), (4.50), (4.54), (4.59), (4.64), (4.66), and (4.68).

# 5 Simple Thermodynamic Systems

## 5.1 Partial Derivatives of Thermodynamic Potentials

Let us consider the partial derivatives of four thermodynamic potentials ($u$, $h$, $f$, and $\varphi$) with respect to the variables $p$, $v$, $T$, and $s$. Obviously, we can find a derivative with respect to one of these variables if another variable, of the remaining three, is kept constant; for example, if the derivative is calculated with respect to $T$, it can be defined for either $p$ constant, $v$ constant, or $s$ constant. We see that each of the named characteristic functions has twelve derivatives in all. Of course, not all are of equal practical importance. Therefore in this section we will focus our attention on the important relations and give the other relations for reference.

5.1.1. We start with the partial derivatives of internal energy. In Chap. 3 we found that, according to (3.26a),

$$\left(\frac{\partial u}{\partial s}\right)_v = T$$

and, according to (3.27a),

$$\left(\frac{\partial u}{\partial v}\right)_s = -p.$$

What are the other relations for the partial derivatives of internal energy?

From Eq. (3.25a)

$$du = T\,ds - p\,dv,$$

taking into account (2.63) and (2.64), we obtain

$$\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial s}{\partial v}\right)_T - p. \qquad (5.1)$$

Combining this with the Maxwell equation (4.3), we find that

$$\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v - p. \qquad (5.2)$$

This relation gives the variation of internal energy with volume in an isothermal process.

In the same manner we can obtain a relation that gives the variation of internal energy with pressure in an isothermal process:

$$\left(\frac{\partial u}{\partial p}\right)_T=T\left(\frac{\partial s}{\partial p}\right)_T-p\left(\frac{\partial v}{\partial p}\right)_T. \tag{5.3}$$

Combining this with the Maxwell equation (4.4), we obtain

$$\left(\frac{\partial u}{\partial p}\right)_T=-T\left(\frac{\partial v}{\partial T}\right)_p-p\left(\frac{\partial v}{\partial p}\right)_T. \tag{5.4}$$

By the method used in (3.25a) with account taken of (2.63), (2.64) and the Maxwell equations, we can easily show that

$$\left(\frac{\partial u}{\partial v}\right)_p=T\left(\frac{\partial p}{\partial T}\right)_s-p, \tag{5.5}$$

$$\left(\frac{\partial u}{\partial p}\right)_v=-T\left(\frac{\partial v}{\partial T}\right)_s, \tag{5.6}$$

$$\left(\frac{\partial u}{\partial p}\right)_s=-p\left(\frac{\partial v}{\partial p}\right)_s, \tag{5.7}$$

$$\left(\frac{\partial u}{\partial s}\right)_p=T-p\left(\frac{\partial T}{\partial p}\right)_s, \tag{5.8}$$

$$\left(\frac{\partial u}{\partial s}\right)_T=T-p\left(\frac{\partial T}{\partial p}\right)_v. \tag{5.9}$$

The quantities $(\partial u/\partial T)_v$, $(\partial u/\partial T)_p$, and $(\partial u/\partial T)_s$ will be considered in Sec. 5.3.

5.1.2. We turn to the partial derivatives of enthalpy. According to (3.29a) and (3.30a),

$$\left(\frac{\partial h}{\partial s}\right)_p=T \quad \text{and} \quad \left(\frac{\partial h}{\partial p}\right)_s=v.$$

Next, Eq. (3.28a)

$$dh = T\,ds + v\,dp$$

together with (2.63) and (2.64) yields

$$\left(\frac{\partial h}{\partial p}\right)_T=T\left(\frac{\partial s}{\partial p}\right)_T+v. \tag{5.10}$$

If we combine this with (4.4), we find that

$$\left(\frac{\partial h}{\partial p}\right)_T=v-T\left(\frac{\partial v}{\partial T}\right)_p. \tag{5.11}$$

This relation gives the variation of enthalpy with pressure in an isothermal process.

In the same manner we obtain a relation giving the dependence of the enthalpy on the volume in an isothermal process:

$$\left(\frac{\partial h}{\partial v}\right)_T=T\left(\frac{\partial s}{\partial v}\right)_T+v\left(\frac{\partial p}{\partial v}\right)_T. \tag{5.12}$$

Combining this with (4.3), we obtain

$$\left(\frac{\partial h}{\partial v}\right)_T=T\left(\frac{\partial p}{\partial T}\right)_v+v\left(\frac{\partial p}{\partial v}\right)_T. \tag{5.13}$$

If we use (3.28a), (2.63), and (2.64) and the Maxwell equations, we can show that

$$\left(\frac{\partial h}{\partial v}\right)_p=T\left(\frac{\partial p}{\partial T}\right)_s, \tag{5.14}$$

$$\left(\frac{\partial h}{\partial p}\right)_v=v-T\left(\frac{\partial v}{\partial T}\right)_s, \tag{5.15}$$

$$\left(\frac{\partial h}{\partial v}\right)_s=v\left(\frac{\partial p}{\partial v}\right)_s, \tag{5.16}$$

$$\left(\frac{\partial h}{\partial s}\right)_v=T-v\left(\frac{\partial T}{\partial v}\right)_s, \tag{5.17}$$

$$\left(\frac{\partial h}{\partial s}\right)_T=T-v\left(\frac{\partial T}{\partial v}\right)_p. \tag{5.18}$$

We will consider the quantities $(\partial h/\partial T)_p$, $(\partial h/\partial T)_v$, and $(\partial h/\partial T)_s$ in Sec. 5.3.

5.1.3. The equations listed in this section, especially (5.11) and (5.2), are of great value for calculating the thermodynamic properties of substances. If we are given the data on the thermal properties of the substance (data on $p$, $v$, $T$-dependence), these equations enable us to find the values of the enthalpy and internal energy and, conversely, to compute the thermal properties of the substance by the given enthalpy and internal energy.

Given the pressure $p$ and temperature $T$, we can find the value of the enthalpy by integrating Eq. (5.11):

$$h(p, T)=h(p_0, T)+\int_{p_0}^{p}\left[v-T\left(\frac{\partial v}{\partial T}\right)_p\right]dp. \tag{5.19}$$

Here $h(p_0, T)$ is the enthalpy of the substance in an initial state with the same temperature but different pressure $p_0$.

Similarly,

$$u(v, T)=u(v_0, T)-\int_{v_0}^{v}\left[T\left(\frac{\partial p}{\partial T}\right)_v-p\right]dv. \tag{5.20}$$

Here $u\,(v_0,\ T)$ is the internal energy of the substance in an initial state with the same temperature $T$ but different volume $v_0$.

If we know the data on the thermal properties of the substance, we can calculate the integrals on the right-hand sides of (5.19) and (5.20); here, of course, in addition to the given data on the $p$, $v$, $T$-dependence we must calculate the derivatives $(\partial v/\partial T)_p$ or $(\partial p/\partial T)_v$. Note that in both cases integration is carried out along an isotherm, namely, Eqs. (5.19) and (5.20) give the variation of the enthalpy and internal energy with $p$ and $v$, respectively, but with $T$ kept constant.

If we take for a point of reference on the given isotherm a caloric quantity ($h$ or $u$) in the ideal-gas state (where the pressure and density of the gas are zero), Eqs. (5.19) and (5.20) become, respectively,

$$h\,(p,\ T)=h_0(T)+\int_0^p\left[v-T\left(\frac{\partial v}{\partial T}\right)_p\right]dp \tag{5.21}$$

and

$$u\,(v,\ T)=u_\infty(T)+\int_\infty^v\left[T\left(\frac{\partial p}{\partial T}\right)_v-p\right]dv. \tag{5.22}$$

Here $h_0\,(T)$ is the enthalpy in the ideal-gas state at temperature $T$, and $u_\infty\,(T)$ is the internal energy in the same state (with an infinite specific volume). We note that the caloric quantities of an ideal gas are functions of temperature alone. The values of $h_0$ and $u_\infty$ can be calculated with a high degree of accuracy by using quantum-statistics methods; the values are obtained on the basis of the data on the molecular structure of the substance.

Equations (5.19) through (5.22) are widely used in calculating the thermodynamic properties of substances via experimental $p$, $v$, $T$ data.

To solve the inverse problem, i.e. to calculate thermal values by the given caloric properties, we transform (5.11) and (5.2) to

$$\left(\frac{\partial h}{\partial p}\right)_T=\left(\frac{\partial\,\frac{v}{T}}{\partial\,\frac{1}{T}}\right)_p \tag{5.23}$$

and

$$\left(\frac{\partial u}{\partial v}\right)_T=-\left(\frac{\partial\,\frac{p}{T}}{\partial\,\frac{1}{T}}\right)_v \tag{5.24}$$

(it is worth noting that $1/T$, $p/T$, and $v/T$ on the right-hand sides of these relations are variables when we consider the Massieu-Planck functions). Integrating these equations, we obtain, respectively,

$$\frac{v(p, T)}{T} = \frac{v(p, T_0)}{T_0} + \int_{T_0}^{T} \left(\frac{\partial h}{\partial p}\right)_T d\frac{1}{T} \tag{5.25}$$

and

$$\frac{p(v, T)}{T} = \frac{p(v, T_0)}{T_0} - \int_{T_0}^{T} \left(\frac{\partial u}{\partial v}\right)_T d\frac{1}{T}. \tag{5.26}$$

Here $v(p, T_0)$ and $p(v, T_0)$ are the values of $v$ and $p$ in an initial state with the same pressure (Eq. (5.25)) or the same volume (Eq. (5.26)) as in the sought state. We note that in Eq. (5.25) we integrate along an isobar, while in (5.26) along an isochore. The partial derivatives of the caloric quantities under the integral sign are calculated by using the existing data on caloric properties of the substance.

The history of thermodynamic calculations of water vapor properties knows cases where the specific volumes of water vapor were calculated using Eq. (5.25) on the basis of experimental data on the enthalpy.

To calculate $u$ by the known $p$ versus $v$ dependence on an isentrope or the known $T$ versus $s$ dependence on an isochore and $h$ by the known $v$ versus $p$ dependence on an isentrope or the known $T$ versus $s$ dependence on an isobar, we can obtain simple relations from Eqs. (3.26a), (3.27a), (3.29a), (3.30a). From (3.27a) we see that

$$u(v, s) = u(v_0, s) - \int_{v_0}^{v} p\, dv, \tag{5.27}$$

from (3.26a) that

$$u(v, s) = u(v, s_0) + \int_{s_0}^{s} T\, ds, \tag{5.28}$$

from (3.30a) that

$$h(p, s) = h(p_0, s) + \int_{p_0}^{p} v\, dp, \tag{5.29}$$

and from (3.29a) that

$$h(p, s) = h(p, s_0) + \int_{s_0}^{s} T\, ds. \tag{5.30}$$

Here $u(v_0, s)$ and $h(p_0, s)$ are, respectively, the internal energy and enthalpy in an initial state on the isentrope under consideration, $u(v, s_0)$ is the internal energy in an initial state on the isochore under consideration, and $h(p, s_0)$ is the enthalpy in an initial state on the isobar under consideration.

5.1.4. We end this section by examining the partial derivatives of the isochoric-isothermal and isobaric-isothermal potentials. According to (3.33a) and (3.32a),

$$\left(\frac{\partial f}{\partial v}\right)_T = -p \text{ and } \left(\frac{\partial f}{\partial T}\right)_v = -s.$$

These give the relations for calculating the value of $f$ by the known $p$ versus $v$ dependence on an isotherm or the known $s$ versus $T$ dependence on an isochore; from (3.33a) we see that

$$f(v, T) = f(v_0, T) - \int_{v_0}^{v} p\, dv, \tag{5.31}$$

while from (3.32a) that

$$f(v, T) = f(v, T_0) - \int_{T_0}^{T} s\, dT. \tag{5.32}$$

Here $f(v_0, T)$ and $f(v, T_0)$ is the isochoric-isothermal potential in an initial state on the isotherm or isobar, respectively. Equation (3.31a)

$$df = -s\, dT - p\, dv$$

together with (2.63), (2.64), and the Maxwell equations yield

$$\left(\frac{\partial f}{\partial p}\right)_T = -p\left(\frac{\partial v}{\partial p}\right)_T, \tag{5.33}$$

$$\left(\frac{\partial f}{\partial T}\right)_p = -p\left(\frac{\partial v}{\partial T}\right)_p - s, \tag{5.34}$$

$$\left(\frac{\partial f}{\partial v}\right)_p = -p - s\left(\frac{\partial T}{\partial v}\right)_p, \tag{5.35}$$

$$\left(\frac{\partial f}{\partial p}\right)_v = -s\left(\frac{\partial T}{\partial p}\right)_v, \tag{5.36}$$

$$\left(\frac{\partial f}{\partial s}\right)_T = -p\left(\frac{\partial T}{\partial p}\right)_v, \tag{5.37}$$

$$\left(\frac{\partial f}{\partial T}\right)_s = -p\left(\frac{\partial v}{\partial T}\right)_s - s, \tag{5.38}$$

$$\left(\frac{\partial f}{\partial s}\right)_p = -\frac{Ts}{c_p} - p\left(\frac{\partial T}{\partial p}\right)_s, \tag{5.39}$$

$$\left(\frac{\partial f}{\partial p}\right)_s = -p\left(\frac{\partial v}{\partial p}\right)_s - s\left(\frac{\partial T}{\partial p}\right)_s, \tag{5.40}$$

$$\left(\frac{\partial f}{\partial v}\right)_s = -p - s\left(\frac{\partial T}{\partial v}\right)_s, \tag{5.41}$$

$$\left(\frac{\partial f}{\partial s}\right)_v = -\frac{Ts}{c_v}. \tag{5.42}$$

According to (3.36a) and (3.35a),

$$\left(\frac{\partial \varphi}{\partial p}\right)_T = v \text{ and } \left(\frac{\partial \varphi}{\partial T}\right)_p = -s.$$

These equations enable us to easily obtain the relations for calculating the value of $\varphi$ by the known $v$ versus $p$ dependence on an isotherm

$$\varphi(p, T) = \varphi(p_0, T) + \int_{p_0}^{p} v\,dp \tag{5.43}$$

or by the known $s$ versus $T$ dependence on an isobar

$$\varphi(p, T) = \varphi(p, T_0) - \int_{T_0}^{T} s\,dp. \tag{5.44}$$

Here $\varphi(p_0, T)$ and $\varphi(p, T_0)$ is the isobaric-isothermal potential in an initial state on an isotherm or isobar, respectively. From Eq. (3.34a)

$$d\varphi = -s\,dT + v\,dp,$$

using (2.63), (2.64), and the Maxwell equations, we easily obtain

$$\left(\frac{\partial \varphi}{\partial v}\right)_T = v\left(\frac{\partial p}{\partial v}\right)_T, \tag{5.45}$$

$$\left(\frac{\partial \varphi}{\partial T}\right)_v = -v\left(\frac{\partial p}{\partial T}\right)_v - s, \tag{5.46}$$

$$\left(\frac{\partial \varphi}{\partial p}\right)_v = v - s\left(\frac{\partial T}{\partial p}\right)_v, \tag{5.47}$$

$$\left(\frac{\partial \varphi}{\partial v}\right)_p = -s\left(\frac{\partial T}{\partial v}\right)_p, \tag{5.48}$$

$$\left(\frac{\partial \varphi}{\partial s}\right)_T = -v\left(\frac{\partial T}{\partial v}\right)_p, \tag{5.49}$$

$$\left(\frac{\partial \varphi}{\partial T}\right)_s = v\left(\frac{\partial p}{\partial T}\right)_s - s, \tag{5.50}$$

$$\left(\frac{\partial \varphi}{\partial s}\right)_v = -\frac{Ts}{c_v} - v\left(\frac{\partial T}{\partial v}\right)_s, \tag{5.51}$$

$$\left(\frac{\partial \varphi}{\partial v}\right)_s = v\left(\frac{\partial p}{\partial v}\right)_s - s\left(\frac{\partial T}{\partial v}\right)_s. \tag{5.52}$$

$$\left(\frac{\partial \varphi}{\partial p}\right)_s = v - s\left(\frac{\partial T}{\partial p}\right)_s, \tag{5.53}$$

$$\left(\frac{\partial \varphi}{\partial s}\right)_p = -\frac{Ts}{c_p}. \tag{5.54}$$

The above relations are employed in an analysis of thermodynamic diagrams when one of the coordinates is $f$ or $\varphi$.

## 5.2 The Gibbs-Helmholtz Equations

5.2.1. Let us write Eqs. (3.41) and (3.44) in the following way:

$$u = f + Ts \tag{5.55}$$

and

$$h = \varphi + Ts. \tag{5.56}$$

If in these relations we substitute $s$, respectively, via (3.32a) and (3.35a), we obtain

$$u = f - T\left(\frac{\partial f}{\partial T}\right)_v \tag{5.57}$$

and

$$h = \varphi - T\left(\frac{\partial \varphi}{\partial T}\right)_p. \tag{5.58}$$

We obtained these equations for mass specific quantities, but the same can be derived for the entire thermodynamic system:

$$U = F - T\left(\frac{\partial F}{\partial T}\right)_V \tag{5.57a}$$

and

$$H = \Phi - T\left(\frac{\partial \Phi}{\partial T}\right)_p. \tag{5.58a}$$

We can easily show that these equations can also be represented thus:

$$u = \left(\frac{\partial \frac{f}{T}}{\partial \frac{1}{T}}\right)_v, \tag{5.59}$$

$$h = \left(\frac{\partial \frac{\varphi}{T}}{\partial \frac{1}{T}}\right)_p, \tag{5.60}$$

and, respectively,

$$U=\left(\frac{\partial\frac{F}{T}}{\partial\frac{1}{T}}\right)_V, \tag{5.59a}$$

$$H=\left(\frac{\partial\frac{\varphi}{T}}{\partial\frac{1}{T}}\right)_p. \tag{5.60a}$$

If we take into account the definitions of the Massieu functions (3.169) and the Planck functions (3.176), we can write Eqs. (5.59a) and (5.60a) thus:

$$U=-\left(\frac{\partial\tilde{F}}{\partial\frac{1}{T}}\right)_V \tag{5.61}$$

and

$$H=-\left(\frac{\partial\tilde{\Phi}}{\partial\frac{1}{T}}\right)_p. \tag{5.62}$$

We see that these relations, respectively, coincide with Eqs. (3.170) and (3.182) derived earlier.

Equations (5.57a) and (5.58a) are known as the Gibbs-Helmholtz equations. They play a significant role in chemical thermodynamics.

5.2.2. Let us examine a thermodynamic process in a complex isochoric-isothermal system. Obviously, for the entire system we can write (5.57a) for the initial state of the process as

$$U_1=F_1-T\left(\frac{\partial F_1}{\partial T}\right)_V, \tag{5.63}$$

and for the final state as

$$U_2=F_2-T\left(\frac{\partial F_2}{\partial T}\right)_V. \tag{5.64}$$

Subtracting termwise (5.64) from (5.63), we obtain

$$-(U_2-U_1)=(F_1-F_2)-T\left(\frac{\partial (F_1-F_2)}{\partial T}\right)_V. \tag{5.65}$$

We recall that in Chap. 3 we considered the amount of work which a complex system can do. The combined equation of the first and second laws of thermodynamics for such a system is of the form (1.24):

$$T\,dS=dU+p\,dV+dL^*, \tag{5.66}$$

where $dL^* = \xi\, dW$. If we combine this equations with (3.7), we obtain

$$dL^* = -dF - S\, dT - p\, dV. \tag{5.67}$$

We see that if the system is under isochoric-isothermal conditions ($V$ and $T$ constant), then

$$dL^*_{V,T} = -dF \tag{5.68}$$

and, hence,

$$L^*_{V,T} = F_1 - F_2. \tag{5.69}$$

Thus, the system performs work (except work of expansion) at the expense of the isochoric-isothermal potential of the system.

Combining (5.65) with (5.69), we find that

$$-\Delta U = L^*_{V,T} - T\left(\frac{\partial L^*_{V,T}}{\partial T}\right)_V, \tag{5.70}$$

where

$$\Delta U = U_2 - U_1 \tag{5.71}$$

is the difference between the internal energies of the system in the final and initial states of the process.

In a similar manner, for a thermodynamic process in a complex isobaric-isothermal system we can write for the initial and final states of the process

$$H_1 = \Phi_1 - T\left(\frac{\partial \Phi_1}{\partial T}\right)_p \tag{5.72}$$

and

$$H_2 = \Phi_2 - T\left(\frac{\partial \Phi_2}{\partial T}\right)_p, \tag{5.73}$$

whence

$$-(H_2 - H_1) = (\Phi_1 - \Phi_2) - T\left(\frac{\partial(\Phi_1 - \Phi_2)}{\partial T}\right)_p. \tag{5.74}$$

Equation (1.24), by employing (3.7) and (3.4), can be transformed to

$$dL^* = -d\Phi - S\, dT + V\, dp, \tag{5.75}$$

which implies that for an isobaric-isothermal system ($p$ and $T$ constant)

$$dL^*_{p,T} = -d\Phi \tag{5.76}$$

and, hence,

$$L^*_{p,T} = \Phi_1 - \Phi_2. \tag{5.77}$$

Thus, the system may perform work at the expense of the isobaric-isothermal potential of the system.

If we combine (5.74) with (5.77), we find that

$$-\Delta H = L^*_{p,T} - T\left(\frac{\partial L^*_{p,T}}{\partial T}\right)_p. \tag{5.78}$$

If the process in the system is accompanied by chemical transformations, $L^*$ is the work performed in the reaction. We know that in chemical thermodynamics the concept of the heat of reaction is widely used; since the heat of isochoric-isothermal reaction $Q_V$ is equal to the change in the internal energy of the system as a result of the reaction.

$$Q_V = U_2 - U_1, \tag{5.79}$$

and the heat of isobaric-isothermal reaction $Q_p$ is equal to the change in the enthalpy of the system as a result of the reaction,

$$Q_p = H_2 - H_1, \tag{5.80}$$

we can write the Gibbs-Helmholtz equations (5.70) and (5.78) thus:

$$-Q_V = L^*_{V,T} - T\left(\frac{\partial L^*_{V,T}}{\partial T}\right)_V \tag{5.81}$$

and

$$-Q_p = L^*_{p,T} - T\left(\frac{\partial L^*_{p,T}}{\partial T}\right)_p. \tag{5.82}$$

The Gibbs-Helmholtz equations in this form find wide application in chemical thermodynamics. For one, they allow the researcher to find such an important characteristic of chemical reaction as the heat of reaction not by means of direct thermochemical measurements but indirectly, by measuring the work $L^*$ performed in the process that accompanies this chemical reaction and by calculating $(\partial L^*/\partial T)$. These equations are also important for analyzing the operation of reversible voltaic cells (see Chap. 9).

5.2.3. Speaking of the Gibbs-Helmholtz equations, it is interesting to examine a group of relations similar to them in structure. We recall that the Gibbs-Helmholtz equations (5.57a) and (5.58a) were obtained as a result of replacing $S$ in Eqs. (3.9) and (3.15) with the help of (3.32) and (3.35), respectively.

Simple analysis shows that we can transform the following relations in a similar manner:

$$H = U + pV, \tag{1.14}$$

$$\Phi = F + pV, \tag{3.16}$$

$$F = U - TS, \tag{3.9}$$

$$\Phi = H - TS. \tag{3.15}$$

We can transform Eqs. (1.14) and (3.16) by substituting the corresponding partial derivatives for $p$ or $V$, and Eqs. (3.9) and (3.15) by substituting the partial derivatives for $T$ or $S$. We have at our disposal the following relations (considered in Chap. 3), which express $p$, $V$, $T$ and $S$ in terms of partial derivatives:

$$T=\left(\frac{\partial U}{\partial S}\right)_V \tag{3.26}$$

and

$$T=\left(\frac{\partial H}{\partial S}\right)_p, \tag{3.29}$$

$$p=-\left(\frac{\partial U}{\partial V}\right)_T \tag{3.27}$$

and

$$p=-\left(\frac{\partial F}{\partial V}\right)_T, \tag{3.33}$$

$$V=\left(\frac{\partial H}{\partial p}\right)_S \tag{3.30}$$

and

$$V=\left(\frac{\partial \Phi}{\partial p}\right)_T, \tag{3.36}$$

$$S=-\left(\frac{\partial F}{\partial T}\right)_V \tag{3.32}$$

and

$$S=-\left(\frac{\partial \Phi}{\partial T}\right)_p. \tag{3.35}$$

We see that replacing $p$, $V$, $T$ and $S$ in Eqs. (1.14), (3.16), (3.9), and (3.15) by the partial derivatives given here yields 16 equations. Two of them (namely, those obtained from (3.9) via (3.32) and from (3.15) via (3.35)) we already know—they are the Gibbs-Helmholtz equations. We can easily obtain the remaining relations of this group. Here we give only the equations similar to the Gibbs-Helmholtz equations in structure.

If we combine (1.14), in succession, with (3.27) and (3.30), we find that

$$H=U-V\left(\frac{\partial U}{\partial V}\right)_S \tag{5.83}$$

and

$$U=H-p\left(\frac{\partial H}{\partial p}\right)_S. \tag{5.84}$$

Replacing $p$ and $V$ (in 3.16) with the help of (3.33) and (3.36), we obtain

$$\Phi = F - V\left(\frac{\partial F}{\partial V}\right)_T \tag{5.85}$$

and

$$F = \Phi - p\left(\frac{\partial \Phi}{\partial p}\right)_T . \tag{5.86}$$

If we substitute (3.26) into (3.9), we find that

$$F = U - S\left(\frac{\partial U}{\partial S}\right)_V , \tag{5.87}$$

while substituting (3.29) into (3.15) yields

$$\Phi = H - S\left(\frac{\partial H}{\partial S}\right)_p . \tag{5.88}$$

We see that for systems with a constant amount of substance these relations can be written in terms of mass specific quantities:

$$h = u - v\left(\frac{\partial u}{\partial v}\right)_s , \tag{5.83a}$$

$$u = h - p\left(\frac{\partial h}{\partial p}\right)_s , \tag{5.84a}$$

$$\varphi = f - v\left(\frac{\partial f}{\partial v}\right)_T , \tag{5.85a}$$

$$f = \varphi - p\left(\frac{\partial \varphi}{\partial p}\right)_T , \tag{5.86a}$$

$$f = u - s\left(\frac{\partial u}{\partial s}\right)_v , \tag{5.87a}$$

$$\varphi = h - s\left(\frac{\partial h}{\partial s}\right)_p . \tag{5.88a}$$

We note in passing that from these relations, which express $p$, $v$, $T$ and $s$ in terms of the corresponding partial derivatives, we can obtain the following useful equations: from (3.26) and (3.29)

$$\left(\frac{\partial U}{\partial S}\right)_V = \left(\frac{\partial H}{\partial S}\right)_p , \tag{5.89}$$

from (3.27) and (3.33)

$$\left(\frac{\partial U}{\partial V}\right)_S = \left(\frac{\partial F}{\partial V}\right)_T , \tag{5.90}$$

from (3.30) and (3.36)

$$\left(\frac{\partial H}{\partial p}\right)_S = \left(\frac{\partial \Phi}{\partial p}\right)_T , \tag{5.91}$$

and from (3.32) and (3.35)

$$\left(\frac{\partial F}{\partial T}\right)_V = \left(\frac{\partial \Phi}{\partial T}\right)_p. \tag{5.92}$$

Incidentally, if by means of these relations we replace the partial derivatives in Eqs. (5.83) through (5.88) and in the Gibbs-Helmholtz equations (5.57a) and (5.58a), we will obtain the remaining relations from the group of above mentioned 16 equations.

We can readily show that just as we can write the Gibbs-Helmholtz equations (5.57a) and (5.58a) in the form (5.59a) and (5.60a), we can write Eqs. (5.83) through (5.88) thus:

$$H = \left(\frac{\partial \frac{U}{V}}{\partial \frac{1}{V}}\right)_S, \tag{5.93}$$

$$U = \left(\frac{\partial \frac{H}{p}}{\partial \frac{1}{p}}\right)_S, \tag{5.94}$$

$$\Phi = \left(\frac{\partial \frac{F}{V}}{\partial \frac{1}{V}}\right)_T, \tag{5.95}$$

$$F = \left(\frac{\partial \frac{\Phi}{p}}{\partial \frac{1}{p}}\right)_T, \tag{5.96}$$

$$F = \left(\frac{\partial \frac{U}{S}}{\partial \frac{1}{S}}\right)_V, \tag{5.97}$$

$$\Phi = \left(\frac{\partial \frac{H}{S}}{\partial \frac{1}{S}}\right)_p. \tag{5.98}$$

Naturally, these relations can be written in terms of mass specific values.

We should note that Eqs. (5.83) through (5.88a) obviously have a certain pedagogical interest: for one, Eqs. (5.84), (5.84a), and (5.83), (5.83a) serve the same purpose for isochoric-isentropic ($V$ and $S$ constant) and isobaric-isentropic ($p$ and $S$ constant) systems, respectively, as the Gibbs-Helmholtz equations do for isochoric-isothermal and isobaric-isothermal systems. But unlike the Gibbs-Helmholtz equations, these equations are insignificant in thermodynamic calculations.

## 5.3 Equations for Heat Capacities

5.3.1. In thermodynamics the (mass specific) heat capacity in the most general form is given by the relationship

$$c_z = T\left(\frac{\partial s}{\partial T}\right)_z, \tag{5.99}$$

where $c_z$ is the heat capacity in a process in which a parameter, $z$, is kept constant.

In this relation we can replace $z$ by any generalized forces and generalized coordinates. The most widespread are the isobaric heat capacity

$$c_p = T\left(\frac{\partial s}{\partial T}\right)_p \tag{5.100}$$

and the isochoric heat capacity

$$c_v = T\left(\frac{\partial s}{\partial T}\right)_p. \tag{5.101}$$

Since according to (2.6)

$$\left(\frac{\partial s}{\partial T}\right)_p = \left(\frac{\partial s}{\partial h}\right)_p \left(\frac{\partial h}{\partial T}\right)_p \tag{5.102}$$

and

$$\left(\frac{\partial s}{\partial T}\right)_v = \left(\frac{\partial s}{\partial u}\right)_v \left(\frac{\partial u}{\partial T}\right)_v \tag{5.103}$$

and from (3.29a) and (3.26a) it follows that

$$\left(\frac{\partial s}{\partial h}\right)_p = \frac{1}{T} \tag{5.104}$$

and

$$\left(\frac{\partial s}{\partial u}\right)_v = \frac{1}{T}, \tag{5.105}$$

we can write (5.100) and (5.101) as

$$c_p = \left(\frac{\partial h}{\partial T}\right)_p \tag{5.106}$$

and

$$c_v = \left(\frac{\partial u}{\partial T}\right)_v. \tag{5.107}$$

5.3.2. In Chap. 7 we will introduce the concepts of the heat capacity along the boundary curve, $c_s$, and the heat capacity of a two-phase mixture, $c_x$.

5.3.3. We can find the equation that links the heat capacities $c_p$ and $c_v$ by the following method.

In accordance with Eq. (2.71) we write

$$\left(\frac{\partial s}{\partial T}\right)_p=\left(\frac{\partial s}{\partial T}\right)_v+\left(\frac{\partial s}{\partial v}\right)_T\left(\frac{\partial v}{\partial T}\right)_p. \tag{5.108}$$

We replace the derivative $(\partial s/\partial v)_T$ via the Maxwell equation (4.3) thus:

$$\left(\frac{\partial s}{\partial v}\right)_T=\left(\frac{\partial p}{\partial T}\right)_v.$$

Combining (5.100) and (5.101), from (5.108) we obtain

$$c_p-c_v=T\left(\frac{\partial p}{\partial T}\right)_v\left(\frac{\partial v}{\partial T}\right)_p. \tag{5.109}$$

Obviously, by means of (2.68) this relations can be written

$$c_p-c_v=-T\left(\frac{\partial p}{\partial v}\right)_T\left(\frac{\partial v}{\partial T}\right)_p^2 \tag{5.110}$$

or

$$c_p-c_v=-T\left(\frac{\partial p}{\partial T}\right)_v^2\left(\frac{\partial v}{\partial p}\right)_T. \tag{5.111}$$

For an ideal gas, whose state is described by the ideal-gas equation

$$pv=RT, \tag{5.112}$$

the above relations imply that

$$c_p-c_v=R, \tag{5.113}$$

which is known as Mayer's formula. Equations (5.109) through (5.111) are often used in calculating the heat capacity $c_v$ in terms of the known values of the heat capacity $c_p$, when it is difficult to determine $c_v$ experimentally.

5.3.4. Taking into account (2.6), we can transform Eq. (5.100) to

$$c_p=T\left(\frac{\partial s}{\partial v}\right)_p\left(\frac{\partial v}{\partial T}\right)_p. \tag{5.114}$$

Combining this with the Maxwell equation (4.2a), we find that

$$c_p=T\left(\frac{\partial p}{\partial T}\right)_s\left(\frac{\partial v}{\partial T}\right)_p. \tag{5.115}$$

In a similar manner, from Eq. (5.101) written as

$$c_v=T\left(\frac{\partial s}{\partial p}\right)_v\left(\frac{\partial p}{\partial T}\right)_v, \tag{5.116}$$

and the Maxwell equation (4.1a) we obtain

$$c_v = -T\left(\frac{\partial p}{\partial T}\right)_v\left(\frac{\partial v}{\partial T}\right)_s. \tag{5.117}$$

Equation (5.115) enables us to reveal the thermodynamic meaning of an empirical relation known in solid-state physics as the Grüneisen relation. It follows from this relation that the bulk thermal expansion coefficient for metals,

$$\alpha = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p, \tag{5.118}$$

in a wide temperature range is uniquely related to their isobaric heat capacities:

$$\alpha = \theta c_p, \tag{5.119}$$

where $\theta$ is a constant characteristic of each metal. The relation between $c_p$ and $\alpha$ is clearly seen from Eq. (5.115), which can be written as

$$\alpha = \frac{1}{vT}\left(\frac{\partial T}{\partial p}\right)_s c_p. \tag{5.120}$$

If we compare (5.120) with (5.119), we see that the quantity $(1/vT)$ $(\partial T/\partial p)_s$ remains constant for those metals for which the Grüneisen relation is valid.

5.3.5. We can obtain one more equation relating $c_p$ and $c_v$ in the following way. If we divide Eq. (5.115) by Eq. (5.117), we have

$$\frac{c_p}{c_v} = -\left(\frac{\partial p}{\partial T}\right)_s\left(\frac{\partial T}{\partial v}\right)_s\left(\frac{\partial v}{\partial T}\right)_p\left(\frac{\partial T}{\partial p}\right)_v. \tag{5.121}$$

Combining this with (2.6) and (2.68), we find that

$$\left(\frac{\partial p}{\partial v}\right)_s = \frac{c_p}{c_v}\left(\frac{\partial p}{\partial v}\right)_T. \tag{5.122}$$

5.3.6. Taking the partial derivative of (5.11)

$$\left(\frac{\partial h}{\partial p}\right)_T = v - T\left(\frac{\partial v}{\partial T}\right)_p$$

with respect to temperature at $p$ constant, we have

$$\frac{\partial^2 h}{\partial p\,\partial T} = -T\left(\frac{\partial^2 v}{\partial T^2}\right)_p. \tag{5.123}$$

Since the value of a mixed derivative does not depend on the order of differentiation, we see that

$$\frac{\partial^2 h}{\partial p\,\partial T} = \left[\frac{\partial}{\partial T}\left(\frac{\partial h}{\partial p}\right)_T\right]_p \left[\frac{\partial}{\partial p}\left(\frac{\partial h}{\partial T}\right)_p\right]_T, \tag{5.124}$$

whence combining (5.124) and (5.106) from (5.123) we obtain

$$\left(\frac{\partial c_p}{\partial p}\right)_T = -T\left(\frac{\partial^2 v}{\partial T^2}\right)_p. \tag{5.125}$$

This relation determines the variation of the heat capacity $c_p$ with the pressure on an isotherm.

In a similar manner, if we differentiate Eq. (5.2) with respect to temperature at $v$ constant,

$$\frac{\partial^2 u}{\partial v\,\partial T} = T\left(\frac{\partial^2 p}{\partial T^2}\right)_v, \tag{5.126}$$

and bear in mind that

$$\frac{\partial^2 u}{\partial v\,\partial T} = \left[\frac{\partial}{\partial T}\left(\frac{\partial u}{\partial v}\right)_T\right]_v = \left[\frac{\partial}{\partial v}\left(\frac{\partial u}{\partial T}\right)_v\right]_T, \tag{5.127}$$

and (5.107), we obtain

$$\left(\frac{\partial c_v}{\partial v}\right)_T = T\left(\frac{\partial^2 p}{\partial T^2}\right)_v, \tag{5.128}$$

which is a relation determining the variation of $c_v$ with the volume on an isotherm.

From (5.125) we see that

$$c_p(p, T) = c_p(p_0, T) - T\int_{p_0}^{p}\left(\frac{\partial^2 v}{\partial T^2}\right)_p dp. \tag{5.129}$$

This relation determines the variation of the heat capacity $c_p$ on an isotherm, with the pressure increasing from $p_0$ to $p$.

In the same manner, from (5.128) there follows the relation that determines the variation of the heat capacity $c_v$ on an isotherm, with specific volume increasing from $v_0$ to $v$:

$$c_v(v, T) = c_v(v_0, T) + T\int_{v_0}^{v}\left(\frac{\partial^2 p}{\partial T^2}\right)_v dv. \tag{5.130}$$

Equations (5.129) and (5.130) are widely employed in calculating the thermodynamic properties of substances. For one, if we know the heat capacity of a substance at low pressures, these equations enable us to calculate the heat capacity at high pressures by the given data on the $p$, $v$, $T$-dependence of the substance. They also allow us to calculate the heat capacities of a condensed phase where, as is known, the value of the heat capacity is affected very little by the pressure, e.g. atmospheric pressure (the experiment for finding the heat capacity at atmospheric pressure is simple and accurate). Due to this, the calculation of the heat capacity of a condensed phase at high pressures is far simpler than a calorimetric experiment with such a state of substance.

The situation is the same when we calculate the heat capacity of a substance in a gaseous phase at high pressures. Now we can write Eqs. (5.129) and (5.130) in a more convenient form

$$c_p(p, T) = c_{p_0}(T) - T\int_0^p \left(\frac{\partial^2 v}{\partial T^2}\right)_p dp \tag{5.131}$$

and

$$c_v(v, T) = c_{v_\infty}(T) + T\int_\infty^v \left(\frac{\partial^2 p}{\partial T^2}\right)_v dv, \tag{5.132}$$

where we denote by $c_{p_0}(T)$ and $c_{v_\infty}(T)$, respectively, the constant-pressure and constant-volume heat capacities of a substance in an ideal-gas state. The first term on the right-hand side of this equation is the part of the heat capacity of a real gas that depends only on temperature (the heat capacity of an ideal gas) and, consequently, independent of pressure; the second term is the part that depends on pressure. In Sec. 5.1 we pointed out that the caloric properties of a substance in the ideal-gas state can be calculated with high accuracy by quantum-statistics methods on the basis of the data on the molecular structure of the substance.

5.3.7. Equations (5.125) and (5.128) enable us to solve the inverse problem; namely, we can calculate thermal quantities in terms of the known values of $c_p$ or $c_v$.

Double integration of Eq. (5.125) yields

$$v(p, T) = v(p, T_0) + \left(\frac{\partial v}{\partial T}\right)_p^{(p,\, T_0)}(T - T_0) - \int_{T_0}^{T}\int_{T_0}^{T} \frac{1}{T}\left(\frac{\partial c_p}{\partial p}\right)_T (dT)^2, \tag{5.133}$$

where $v(p, T)$ is the specific volume of a substance at a given pressure $p$ and temperature $T$, and $v(p, T_0)$ and $(\partial v/\partial T)_p^{(p, T_0)}$ are the quantities in the initial state with the same pressure $p$ but different temperature $T_0$.

In a similar manner double integration of (5.128) yields

$$p(v, T) = p(v, T_0) + \left(\frac{\partial p}{\partial T}\right)_v^{(v,\, T_0)}(T - T_0) - \int_{T_0}^{T}\int_{T_0}^{T} \frac{1}{T}\left(\frac{\partial c_v}{\partial v}\right)_T (dT)^2, \tag{5.134}$$

where $p\,(v,\ T)$ is the pressure at the given specific volume and temperature, and $p\,(v,\ T_0)$ and $(\partial p/\partial T)_v^{(v, T_0)}$ are the quantities in the initial state with the same volume $v$ but different temperature $T_0$.

We note that these relations are interesting not only from the theoretical point of view. In 1932 A. Knoblaugh and others compiled tables of water vapor specific volumes on the basis of the data (available at that time) on the isobaric heat capacity of water vapor; it was the most unusual case in the history of thermodynamic investigations when scientists had data on the heat capacity $c_p$ that was more accurate than that on water vapor specific volumes.

5.3.8. By the known values of the heat capacities $c_p$ and $c_v$ we can easily determine the change in the enthalpy and internal energy of a substance for $p$ and $v$ constant: from (5.106) and (5.107) we see that

$$h\,(p,\ T)=h\,(p,\ T_0)+\int\limits_{T_0}^{T} c_p\,dT \tag{5.135}$$

and

$$u\,(v,\ T)=u\,(v,\ T_0)+\int\limits_{T_0}^{T} c_v\,dT, \tag{5.136}$$

where $h\,(p,\ T_0)$ and $u\,(v,\ T_0)$ are, respectively, the enthalpy and internal energy of a substance in an initial state with the same pressure and specific volume but different temperature.

We see that the values of $h_0\,(T)$ and $u_\infty\,(T)$ from Eqs. (5.21) and (5.22) are related to $c_{p0}\,(T)$ and $c_{v_\infty}\,(T)$ by the following equations:

$$h_0(T)=h_0(0)+\int\limits_{0}^{T} c_{p_0}(T)\,dT \tag{5.137}$$

and

$$u_\infty(T)=u_\infty(0)+\int\limits_{0}^{T} c_{v_\infty}(T)\,dT. \tag{5.138}$$

Here $h_0$ (0) and $u_\infty$ (0) are, respectively, the enthalpy and internal energy of an ideal gas at $T = 0$ K; this temperature is usually taken as the reference point for $h_0$ and $u_\infty$.

5.3.9. To compute the derivatives $(\partial u/\partial T)_s$ and $(\partial h/\partial T)_s$ we give two more equations related to the heat capacities $c_v$ and $c_p$.

In accordance with (2.71) we can write

$$\left(\frac{\partial u}{\partial T}\right)_s=\left(\frac{\partial u}{\partial T}\right)_v+\left(\frac{\partial u}{\partial v}\right)_T\left(\frac{\partial v}{\partial T}\right)_s \tag{5.139}$$

and

$$\left(\frac{\partial h}{\partial T}\right)_s=\left(\frac{\partial h}{\partial T}\right)_p+\left(\frac{\partial h}{\partial p}\right)_T\left(\frac{\partial h}{\partial T}\right)_s. \tag{5.140}$$

Combining these relations with (5.2) and (5.11), respectively, we obtain

$$\left(\frac{\partial u}{\partial T}\right)_s = c_v + \left[T\left(\frac{\partial p}{\partial T}\right)_v - p\right]\left(\frac{\partial v}{\partial T}\right)_s \tag{5.141}$$

and

$$\left(\frac{\partial h}{\partial T}\right)_s = c_p + \left[v - T\left(\frac{\partial v}{\partial T}\right)_p\right]\left(\frac{\partial p}{\partial T}\right)_s . \tag{5.142}$$

5.3.10. Finally, we write (5.42) and (5.54) as

$$c_v = -Ts\left(\frac{\partial s}{\partial f}\right)_v \tag{5.143}$$

and

$$c_p = -Ts\left(\frac{\partial s}{\partial \varphi}\right)_p . \tag{5.144}$$

These interesting equations relate isochoric and isobaric heat capacities to the derivatives that characterize the variations of the isochoric-isothermal (for $v$ constant) and isobaric-isothermal (for $p$ constant) potentials with entropy.

## 5.4 Equations for Entropy

5.4.1. The variation in entropy with the thermal quantities ($p$, $v$, $T$) is given by the Maxwell equations discussed in Chap. 4

$$\left(\frac{\partial s}{\partial p}\right)_v = -\left(\frac{\partial v}{\partial T}\right)_s , \tag{4.1a}$$

$$\left(\frac{\partial s}{\partial v}\right)_p = \left(\frac{\partial p}{\partial T}\right)_s , \tag{4.2a}$$

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v , \tag{4.3}$$

$$\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p , \tag{4.4}$$

and the relationships

$$\left(\frac{\partial s}{\partial T}\right)_p = \frac{c_p}{T} , \tag{5.100a}$$

$$\left(\frac{\partial s}{\partial T}\right)_v = \frac{c_v}{T} . \tag{5.101a}$$

5.4.2. Equations (4.1a) and (5.101a) imply that the change in entropy in an isochoric process is defined by the equation

$$s(v, p_2) - s(v, p_1) = -\int_{p_1}^{p_2}\left(\frac{\partial v}{\partial T}\right)_s dp \tag{5.145}$$

or

$$s(v, T_2) - s(v, T_1) = \int_{T_1}^{T_2} \frac{c_v}{T}\, dT; \qquad (5.146)$$

here $p_1$ and $T_1$ are the state parameters at the initial point of the isochoric process under consideration, and $p_2$ and $T_2$ at the terminal point of the process. We see that the changes in entropy, calculated via (5.145) and via (5.146), are the same. This becomes obvious, for instance, if we compare the right-hand sides of these equations combined with (5.117).

Similarly, from (4.2a) and (5.100a) it follows that the change in entropy in an isobaric process is defined by the equation

$$s(p, v_2) - s(p, v_1) = \int_{v_1}^{v_2} \left(\frac{\partial p}{\partial T}\right)_s dv \qquad (5.147)$$

or

$$s(p, T_2) - s(p, T_1) = \int_{T_1}^{T_2} \frac{c_p}{T}\, dT; \qquad (5.148)$$

here $v_1$ and $T_1$ are the parameters at the initial point, and $v_2$ and $T_2$ at the terminal point of the isobaric process under consideration. From (5.115) we see that the right-hand sides of these relations are equal.

From (4.3) and (4.4) we finally obtain for the change in entropy in an isothermal process

$$s(T, v_2) = s(T, v_1) = \int_{v_1}^{v_2} \left(\frac{\partial p}{\partial T}\right)_v dv \qquad (5.149)$$

or

$$s(T, p_2) - s(T, p_1) = -\int_{p_1}^{p_2} \left(\frac{\partial v}{\partial T}\right)_p dp, \qquad (5.150)$$

here $p_1$ and $v_1$ determine the initial point of the isothermal process, $p_2$ and $v_2$ the terminal point of the process. We see from (2.68) that the right-hand sides of these equations are equal.

5.4.3. From (1.27a)

$$T\, ds = du + pdv$$

it follows that

$$\left(\frac{\partial s}{\partial v}\right)_u = \frac{p}{T}, \qquad (5.151)$$

while from (3.28a) written as

$$T\,ds = dh - v\,dp \tag{5.152}$$

it follows that

$$\left(\frac{\partial s}{\partial p}\right)_h = -\frac{v}{T}. \tag{5.153}$$

These relationships are used for calculating the change in entropy in processes with $u$ constant and $h$ constant, respectively. From (5.151) we see that

$$s(u, v_2) - s(u, v_1) = \int_{v_1}^{v_2} \frac{p}{T}\,dv \tag{5.154}$$

(integration is carried out along the line $u$ = const), and from (5.153)

$$s(h, p_2) - s(h, p_1) = -\int_{p_1}^{p_2} \frac{v}{T}\,dp \tag{5.155}$$

(integration is carried out along the line $h$ = const).

Finally, from (5.105)

$$\left(\frac{\partial s}{\partial h}\right)_v = \frac{1}{T}$$

and (5.104)

$$\left(\frac{\partial s}{\partial h}\right)_p = \frac{1}{T}$$

it follows that

$$s(u_2, v) - s(u_1, v) = \int_{u_1}^{u_2} \frac{1}{T}\,du \tag{5.156}$$

and

$$s(h_2\, p) - s(h_1, p) = \int_{h_1}^{h_2} \frac{1}{T}\,dh. \tag{5.157}$$

In the first relation the integral is taken along an isochore and in the second along an isobar.

## 5.5 Other Important Partial Derivatives of Thermodynamic Functions

5.5.1. Let us formulate some important relationships that determine the derivative $(\partial v/\partial p)_s$ and the inverse, $(\partial p/\partial v)_s$.

In accordance with (2.71) we can write

$$\left(\frac{\partial v}{\partial p}\right)_s = \left(\frac{\partial v}{\partial p}\right)_T + \left(\frac{\partial v}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_s. \tag{5.158}$$

In accordance with the Maxwell equation (4.2),

$$\left(\frac{\partial T}{\partial p}\right)_s=\left(\frac{\partial v}{\partial s}\right)_p.$$

Here the derivative $(\partial v/\partial s)_p$, according to (2.6), can be written as

$$\left(\frac{\partial v}{\partial s}\right)_p=\left(\frac{\partial v}{\partial T}\right)_p\left(\frac{\partial T}{\partial s}\right)_p, \tag{5.159}$$

or, combined with (5.100a),

$$\left(\frac{\partial v}{\partial s}\right)_p=\frac{T}{c_p}\left(\frac{\partial v}{\partial T}\right)_p. \tag{5.160}$$

If we combine (4.2) with (5.160), from (5.158) we obtain

$$\left(\frac{\partial v}{\partial p}\right)_s=\left(\frac{\partial v}{\partial p}\right)_T+\frac{T}{c_p}\left(\frac{\partial v}{\partial T}\right)_p^2. \tag{5.161}$$

In a similar manner we can write

$$\left(\frac{\partial p}{\partial v}\right)_s=\left(\frac{\partial p}{\partial v}\right)_T+\left(\frac{\partial p}{\partial T}\right)_v\left(\cancel{\frac{Tp}{\partial v}}\right)_s\cdot\left.\frac{\partial T}{\partial v}\right)_s \tag{5.162}$$

From the Maxwell equation (4.1)

$$\left(\frac{\partial T}{\partial v}\right)_s=-\left(\frac{\partial p}{\partial s}\right)_v,$$

where, in accordance with (2.6), we can write

$$\left(\frac{\partial p}{\partial s}\right)_s=\left(\frac{\partial p}{\partial T}\right)_v\left(\frac{\partial T}{\partial s}\right)_v, \tag{5.163}$$

we find, combining this equation with (5.101a), that

$$\left(\frac{\partial p}{\partial s}\right)_v=-\frac{T}{c_v}\left(\frac{\partial p}{\partial T}\right)_v, \tag{5.164}$$

and from (5.135), (4.1) and (5.137) we obtain

$$\left(\frac{\partial p}{\partial v}\right)_s=\left(\frac{\partial p}{\partial v}\right)_T-\frac{T}{c_v}\left(\frac{\partial p}{\partial T}\right)_v. \tag{5.165}$$

Equations (5.161) and (5.165) are rarely mentioned in the literature. But these relations are very useful for certain thermodynamic calculations, as we will show in Chap. 7.

5.5.2. In thermodynamics we use the concept of the so-called thermal coefficients which are defined thus:

the coefficient of isothermal compressibility

$$\beta_T=-\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T, \tag{5.166}$$

the coefficient of adiabatic compressibility

$$\beta_s = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_s, \tag{5.167}$$

and the bulk thermal expansion coefficient (which was defined in Sec. 5.3, Eq. (5.118))

$$\alpha = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p.$$

5.5.3. The Joule-Thomson coefficient is defined by the relation

$$\mu = \left(\frac{\partial T}{\partial p}\right)_h. \tag{5.168}$$

This quantity shows the variation of fluid temperature with pressure in adiabatic throttling (we note that the adiabatic throttling process occurs at constant enthalpy).

Obviously, in accordance with (2.67) the derivative $(\partial T/\partial p)_h$ can be written thus:

$$\left(\frac{\partial T}{\partial p}\right)_h = -\left(\frac{\partial T}{\partial h}\right)_p\left(\frac{\partial h}{\partial p}\right)_T. \tag{5.169}$$

If we replace the derivatives on the right-hand side of this equation by (5.106) and (5.11), we obtain a relation that defines the value of the Joule-Thomson coefficient:

$$\mu = \frac{1}{c_p}\left[T\left(\frac{\partial v}{\partial T}\right)_p - v\right]. \tag{5.170}$$

We know that adiabatic throttling (for the states where $\mu > 0$, which is the region below the Joule-Thomson inversion curve) is used for gas cooling. An effective method of gas cooling is reversible adiabatic (i.e. isentropic) expansion of a gas (without external work); this effect is defined by the coefficient of adiabatic expansion

$$\mu_s = \left(\frac{\partial T}{\partial p}\right)_s. \tag{5.171}$$

From the obvious relation

$$\left(\frac{\partial T}{\partial p}\right)_s\left(\frac{\partial p}{\partial s}\right)_T\left(\frac{\partial s}{\partial T}\right)_p = -1 \tag{5.172}$$

combined with (5.100) and the Maxwell equation (4.4a), we see that

$$\mu_s = \frac{T}{c_p}\left(\frac{\partial v}{\partial T}\right)_p. \tag{5.173}$$

Comparing $\mu$ and $\mu_s$ enables us to establish which of the two methods of gas cooling is more effective. From (5.170) and (5.173) we see that

$$\mu_s - \mu = v/c_p. \tag{5.174}$$

Therefore, always

$$\mu_s > \mu, \tag{5.175}$$

i.e. adiabatic expansion is the more effective method of gas cooling.

5.5.4. We know that in the process of adiabatic expansion of a real gas into vacuum (the Joule process), with the internal energy kept constant, the quantity $(\partial T/\partial v)_u$ is of great importance. It shows how the gas temperature changes in the process and can be defined in the following way: according to (2.67) we can write

$$\left(\frac{\partial T}{\partial v}\right)_u = -\left(\frac{\partial T}{\partial u}\right)_v \left(\frac{\partial u}{\partial v}\right)_T. \tag{5.176}$$

Combining this with (5.107) and (5.2), we obtain

$$\left(\frac{\partial T}{\partial v}\right)_u = \frac{1}{c_v}\left[p - T\left(\frac{\partial p}{\partial T}\right)_v\right]. \tag{5.177}$$

## 5.6 The Differential Equation of an Isentrope. The Laplace Equation

5.6.1. Let us formulate the differential equation for an isentropic process. Equation (3.28a)

$$dh = T\,ds - v\,dp$$

yields for the process under consideration

$$\left(\frac{\partial h}{\partial u}\right)_s = -v\left(\frac{\partial p}{\partial u}\right)_s. \tag{5.178}$$

Combining this with (5.7), we obtain

$$\left(\frac{\partial h}{\partial u}\right)_s = -\frac{v}{p}\left(\frac{\partial p}{\partial v}\right)_s, \tag{5.179}$$

which is the equation of an adiabatic (isentrope).

Let us introduce the notation

$$k = \left(\frac{\partial h}{\partial u}\right)_s. \tag{5.180}$$

Here $k$ is the exponent of the isentropic process (or adiabatic exponent). Then (5.179) becomes

$$k = -\frac{v}{p}\left(\frac{\partial p}{\partial v}\right)_s. \tag{5.181}$$

This relationship is widely used to calculate the adiabatic exponent for a substance in various states.

5.6.2. If we combine (5.122) with (5.181), we find that

$$k = -\frac{c_p}{c_v}\,\frac{v}{p}\left(\frac{\partial p}{\partial v}\right)_T. \tag{5.182}$$

From this and (5.108) it follows that for an ideal gas

$$k=\frac{c_p}{c_v}. \tag{5.183}$$

Next, using Eq. (5.165), we can write (5.181) thus:

$$k=\frac{v}{p}\left[\frac{T}{c_v}\left(\frac{\partial p}{\partial T}\right)_v^2-\left(\frac{\partial p}{\partial v}\right)_T\right]. \tag{5.184}$$

5.6.3. Obviously, Eq. (5.181) can also be written in the following form:

$$k=-\left(\frac{\partial \ln p}{\partial \ln v}\right)_s. \tag{5.185}$$

Integrating this relation between the points *1* and *2* on an isentrope, we obtain

$$\ln\frac{p_2}{p_1}=-\int_{v_1}^{v_2} k d\ln v. \tag{5.186}$$

The value of the adiabatic exponent $k$ varies with the state parameters; it differs considerably for different phases of the substance. If the adiabatic exponent $k$ is kept constant throughout a multitude of the system's states (between the points *1* and *2*), it is clear from (5.186) that

$$\ln\frac{p_2}{p_1}=-k\ln\frac{v_2}{v_1}. \tag{5.187}$$

From this relation it follows, for one, that

$$pv^k=\text{const}. \tag{5.188}$$

This relation (which is valid provided the adiabatic exponent is kept constant) is known as the Poisson adiabatic equation. But if in the range of states under consideration the adiabatic exponent varies with the state parameters and we know the behaviour of $k$ on an adiabatic, we can calculate $p_2$ in terms of the given $p_1$, $v_1$ and $v_2$ by Eq. (5.186).

5.6.4. The thermodynamic velocity of sound, $a$, is defined by the Laplace equation

$$a=\sqrt{\left(\frac{\partial p}{\partial \rho}\right)_s}, \tag{5.189}$$

where $\rho$ is the density of the substance; since

$$\rho=1/v, \tag{5.190}$$

we have

$$a=\sqrt{-v^2\left(\frac{\partial p}{\partial v}\right)_s}. \tag{5.191}$$

This combined with (5.181) yields

$$a = \sqrt{kpv}, \tag{5.192}$$

and combined with (5.165) also yields

$$a = v\sqrt{\frac{T}{c_v}\left(\frac{\partial p}{\partial T}\right)_v^2 - \left(\frac{\partial p}{\partial v}\right)_T}. \tag{5.193}$$

## 5.7 Basic Thermodynamic Equations for Flow Processes

5.7.1. In Chap. 1 we noted that the equation of the first law of thermodynamics for the flow of a liquid or gas is written thus (Eq. (1.16)):

$$dq = dh + w\,dw + g\,dz + dl_{\text{tech}} + dl_{\text{diss}},$$

where $w$ is the flow velocity, $z$ the height, $l_{\text{tech}}$ the technical work done by the flow, $l_{\text{diss}}$ the dissipative work (e.g. the work done by the flow in overcoming frictional forces), and $g$ the acceleration of gravity.

We recall that the heat $q$ in Eq. (1.16) consists of two parts: the heat brought into the flow from outside (or rejected from it to the surroundings), $q_{\text{ext}}$, and the dissipative heat, $q_{\text{diss}}$; and that $q_{\text{diss}}$ is equivalent to $l_{\text{diss}}$. Hence, we can write Eq. (1.16) in the form (1.18):

$$dq_{\text{ext}} = dh + w\,dw + g\,dz + dl_{\text{tech}}.$$

This equation is valid both with and without friction in the flow.

5.7.2. Let us consider a particular case of a flow, when a portion of the flow considered is on one level and, therefore, $dz = 0$ and when there is no technical work and this work is not brought into the flow from outside ($dl_{\text{tech}} = 0$). For this particular case Eq. (1.18) assumes the form

$$dq_{\text{ext}} = dh + w\,dw. \tag{5.194}$$

For the majority of technologically important problems the case of greatest interest is that of adiabatic flow, i.e. a flow without supply and rejection of heat from outside ($dq_{\text{ext}} = 0$). For this case (5.194) assumes the form

$$dh + w\,dw = 0. \tag{5.195}$$

This implies that if an adiabatic flow accelerates ($dw > 0$), its enthalpy decreases ($dh < 0$), and vice versa. Hence, the acceleration of an adiabatic flow occurs at the expense of its enthalpy.

Further, Eq. (5.194) combined with (1.14a) can be written as

$$dq_{\text{ext}} = du + d(pv) + w\,dw. \tag{5.196}$$

We compare this relation with the equation of the first law of thermodynamics in the ordinary form (1.10a)

$$dq = du + pdv.$$

We see that Eqs. (5.196) and (1.10a) are essentially the same, only expressing differently the first law of thermodynamics: (1.10a) represents the law in the most general form (for simple systems) while (5.196) specifies the particular case where the simple thermodynamic system is a fluid in flow. Then

$$pdv = d\,(pv) + wdw. \tag{5.197}$$

Taking into account

$$d\,(pv) = pdv + vdp, \tag{5.198}$$

we find that

$$wdw = -\,vdp. \tag{5.199}$$

The above derivation shows that Eq. (5.199) is valid for a flow in any conditions of addition (rejection) of heat: when there is no friction, the flow is horizontal and the technical work is zero. This equation implies that if the pressure drops along the path of flow ($dp < < 0$), the flow velocity increases ($dw > 0$) and vice versa.

Finally, from (5.195) and (5.199) we see that

$$dh = vdp. \tag{5.200}$$

Since (5.195) is valid only for adiabatic flow without friction, the same is true for (5.200).

Equations (5.194), (5.195), (5.199), and (5.200) are the basic relations for horizontal flow without the technical work.

5.7.3. A differential equation very important in an analysis of adiabatic flow (horizontal flow without technical work) can be obtained in the following manner.

The continuity of the flow implies that for a stationary flow the fluid flow rate $G$ is the same in any cross section of the flow; $G = = \text{const}$. Since for a flow in a channel of any cross section

$$G = w\Sigma/v, \tag{5.201}$$

where $\Sigma$ is the area of the channel's cross section, we have for $G$ constant

$$\frac{d\Sigma}{\Sigma} = \frac{dv}{v} - \frac{dw}{w}. \tag{5.202}$$

In hydrodynamics this relationship is termed the *continuity equation.*

For the case under consideration (horizontal flow without technical work) this equation can be transformed in the following way. From (5.199) we see that

$$\frac{dw}{w} = -\frac{v}{w}\,dp \tag{5.203}$$

(note that (5.199) is valid only for the flow without friction).

Equation (5.181) for adiabatic flow ($s$ is const) can be written as

$$\frac{dv}{v} = -\frac{1}{kp}\,dp. \tag{5.204}$$

If we substitute (5.203) and (5.204) into (5.202) and assume that in accordance with the Laplace equation (5.192)

$$kpv = a^2, \tag{5.205}$$

we obtain

$$\frac{d\Sigma}{\Sigma} = \frac{d^2 - w^2}{kpw^2}\,dp, \tag{5.206}$$

or, which is the same,

$$\frac{d\Sigma}{\Sigma} = \frac{1}{kp}\left(\frac{1}{M^2} - 1\right) dp. \tag{5.207}$$

Here $M = w/a$ is the Mach number (the ratio of the flow velocity to the local speed of sound). This equation relates the change in the area of the channel's cross section (for adiabatic horizontal flow without friction and technical work) to the change in flow pressure and to the Mach number. If in (5.207) we replace $dp$ by (5.204) and combine the result with (5.205), we obtain an equation that shows the variation of the area of the channel's cross section with the flow velocity and M:

$$\frac{d\Sigma}{\Sigma} = (M^2 - 1)\frac{dw}{w}. \tag{5.208}$$

Equations (5.207) and (5.208) enable us to analyze a horizontal adiabatic flow without the technical work in channels with variable cross sections.

For subsonic speeds ($M < 1$), the convergence of a channel ($d\Sigma < 0$) corresponds to a decrease in pressure in the flow along the channel ($dp < 0$). Here the velocity of a fluid increases ($dw > 0$) as the channel converges. If the channel diverges ($d\Sigma > 0$), the pressure along it increases ($dp > 0$) and the velocity decreases ($dw < 0$).

For supersonic speeds ($M > 1$), the sign of these effects changes; namely, if the channel converges ($d\Sigma < 0$), the pressure in the flow increases ($dp > 0$) and the velocity of the fluid decreases ($dw < 0$), while if the channel diverges ($d\Sigma > 0$), the pressure decreases along the flow ($dp < 0$) and the velocity increases ($dw > 0$).

These modes of acceleration and deceleration of a flow are used in well-known devices: subsonic and supersonic adiabatic nozzles and diffusers.

5.7.4. Let us now examine a case important from the standpoint of practice of adiabatic flow without friction and external work, the case of the flow of an incompressible fluid.

Since the flow takes place at $dq = 0$, $l_{\text{diss}} = 0$, and $l_{\text{tech}} = 0$, we can write Eq. (1.16) as

$$dh + wdw + gdz = 0. \tag{5.209}$$

From the equation of the first law of thermodynamics (1.10a)

$$dq = du + pdv$$

we can see that in adiabatic conditions

$$du = -pdv, \tag{5.210}$$

and for an incompressible medium ($v$ is constant) in adiabatic conditions

$$du = 0. \tag{5.211}$$

Next, combining (1.14a) with (5.209), we find that

$$du + pdv + vdp + wdw + gdz = 0. \tag{5.212}$$

If we bear in mind that for an incompressible medium $dv = 0$ and combine this relation with (5.211), we obtain for this particular case of an incompressible fluid flow

$$vdp + wdw + gdz = 0, \tag{5.213}$$

or, since $v = 1/\rho$,

$$dp + \rho wdw + \rho gdz = 0. \tag{5.314}$$

This equation, which is written for the first law of thermodynamics for the adiabatic flow of an incompressible fluid (without friction), is known as *Bernoulli's equation* (in differential form); in hydrodynamics this equation is derived from Newton's laws.

5.7.5. In Sections 5.7.2 through 5.7.4 we considered the cases of flow important for practice; but these are only particular cases. In all these cases we assumed that, first, technical work is not performed in the flow and is not done on it and, second, the flow is horizontal (except the case considered in Sec. 5.7.4), i.e. $dz = 0$. Here Eq. (5.195) is valid only for adiabatic flow, (5.199) for flow without friction, (5.200) for adiabatic flow without friction, (5.207) for adiabatic flow, and (5.208) for adiabatic flow without friction.

Let us now formulate the equation in the most general case, i.e. for a flow without the restrictions imposed on the above-mentioned relations. To this end we examine the differential equation of the first law of thermodynamics for a flow in its general form, (1.16), and express $dh$ via (1.14a):

$$dq = du + d(pv) + wdw + gdz + dl_{\text{tech}} + dl_{\text{diss}}. \tag{5.215}$$

Replacing $dq$ by (1.10a), we obtain

$$vdp + wdw + gdz + dl_{\text{tech}} + dl_{\text{diss}} = 0. \tag{5.216}$$

(We note that for the case of horizontal flow without friction and technical work this relation is transformed to (5.199).)

The differential $dp$ from Eq. (5.216) can be written, in accordance with (2.24), as

$$dp = \left(\frac{\partial p}{\partial v}\right)_s dv + \left(\frac{\partial p}{\partial s}\right)_v ds. \tag{5.217}$$

Next, according to (4.1),

$$\left(\frac{\partial p}{\partial s}\right)_v = -\left(\frac{\partial T}{\partial v}\right)_s,$$

while according to (2.6) the derivative $(\partial T/\partial v)_s$ can be written as

$$\left(\frac{\partial T}{\partial v}\right)_s = \left(\frac{\partial T}{\partial p}\right)_s \left(\frac{\partial p}{\partial v}\right)_s. \tag{5.218}$$

The derivative $(\partial T/\partial p)_s$ can then be replaced via Eq. (5.115), which can be written as

$$\left(\frac{\partial T}{\partial p}\right)_s = \frac{T}{c_p}\left(\frac{\partial v}{\partial T}\right)_p. \tag{5.219}$$

If we combine (5.218) with (5.219), we find that (4.1) can be transformed to

$$\left(\frac{\partial p}{\partial s}\right)_v = -\frac{T}{c_p}\left(\frac{\partial v}{\partial T}\right)_p \left(\frac{\partial p}{\partial v}\right)_s. \tag{5.220}$$

From (5.217) it then follows that

$$dp = \left(\frac{\partial p}{\partial v}\right)_s \left[dv - \frac{T}{c_p}\left(\frac{\partial v}{\partial T}\right)_p ds\right]. \tag{5.221}$$

From (5.191) we see that

$$\left(\frac{\partial p}{\partial v}\right)_s = -\left(\frac{a}{v}\right)^2. \tag{5.222}$$

Since according to (1.17) for the flow

$$dq = dq_{\text{ext}} + dq_{\text{diss}},$$

taking into account (1.20a)

$$dq = T\,ds$$

we can write[1]

$$ds = \frac{dq_{\text{ext}} + dq_{\text{diss}}}{T}. \tag{5.223}$$

Finally, we express the differential $dv$ from (5.221) in terms of the continuity equation (5.195):

$$dv = v\left(\frac{d\Sigma}{\Sigma} + \frac{dw}{w}\right). \tag{5.224}$$

If we consider Eqs. (5.222) through (5.224) and notation (5.118), from (5.221) we obtain

$$vdp = -a^2\left[\frac{d\Sigma}{\Sigma} + \frac{dw}{w} - \frac{\alpha}{c_p}\left(dq_{\text{ext}} + dq_{\text{diss}}\right)\right]. \tag{5.225}$$

Substituting this relation into (5.216) and taking into account that $q_{\text{diss}} = l_{\text{diss}}$ and $w/a = M$, we obtain

$$(M^2 - 1)\frac{dw}{w} = \frac{d\Sigma}{\Sigma} - \frac{\alpha}{c_p}\,dq_{\text{ext}} - \frac{1}{a^2}\,dl_{\text{tech}} - \left(\frac{\alpha}{c_p} + \frac{1}{a^2}\right) dl_{\text{diss}} - \frac{g}{a^2}\,dz. \tag{5.226}$$

This equation, obtained by L. Vulis, enables us to draw interesting conclusions about possible means of accelerating the flow.

If $q_{\text{ext}} = 0$, $l_{\text{tech}} = 0$, $l_{\text{diss}} = 0$, and $z = \text{const}$, Eq. (5.226) is transformed to (5.208) which describes the mechanism of change of the flow velocity in a standard nozzle (sometimes called geometrical nozzle) discussed in Sec. 5.7.3.

If the cross section of the channel is constant ($\Sigma$ is constant) and $l_{\text{tech}} = 0$, $l_{\text{diss}} = 0$, and $z = \text{const}$, but there is an influx or rejection of heat, Eq. (5.226) implies that

$$(M^2 - 1)\frac{dw}{w} = -\frac{\alpha}{c_p}\,dq_{\text{ext}}. \tag{5.227}$$

Since always $c_p > 0$ and, as a rule, $\alpha > 0$, it follows that at subsonic flow velocities ($M < 1$) addition of heat to the flow ($dq_{\text{ext}} > 0$) results in acceleration ($dw > 0$), while rejection of heat from the flow results in deceleration. Correspondingly, in supersonic flow ($M > 1$) addition of heat results in deceleration and rejection results in acceleration. The principle of a heat nozzle, a channel in which

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[1] Concerning Eq. (5.223) the following question may arise. In Chap. 1 we noted that Eq. (1.20a) is valid only for reversible processes. But processes of energy dissipation, as a result of which the heat $q_{\text{diss}}$ is liberated, are essentially irreversible. What is the meaning of Eq. (5.223) then? The answer is that it is valid for a reversible process; here we tacitly assume that $q_{\text{diss}}$ is not the heat liberated as a result of friction but the heat equal in value to $q_{\text{diss}}$, which is reversibly supplied to the flow from the surrounding medium (apart from the heat $q_{\text{ext}}$ brought in from the medium).

addition or rejection of heat results in acceleration of the flow, is based on these conclusions.

If $\Sigma$ is constant and $q_{\text{ext}} = 0$, $l_{\text{diss}} = 0$, and $z = \text{const}$ and the flow performs technical work (or this work is performed on the flow), from (5.226) we obtain

$$(M^2 - 1)\frac{dw}{w} = -\frac{1}{a^2}\,dl_{\text{tech}}. \tag{5.228}$$

We see that in these conditions a subsonic flow ($M < 1$) performs technical work (for instance, rotating a turbine) and is accelerated ($dw > 0$). Correspondingly, if technical work is performed on the flow, this results in deceleration of the flow. In a supersonic flow ($M > 1$) the processes are reversed. These principles are utilized in the so-called mechanical nozzle, a heat-insulated channel in which a subsonic flow is accelerated at the expense of the work done on the turbine-wheel blades and a supersonic flow is accelerated due to a blower rotated by an external source.

If $\Sigma$ is constant and $q_{\text{ext}} = 0$, $l_{\text{tech}} = 0$, and $l_{\text{diss}} = 0$ but the channel is not horizontal ($dz \neq 0$), then from (5.226) it follows that

$$(M^2 - 1)\frac{dw}{w} = -\frac{g}{a^2}\,dz. \tag{5.229}$$

This relation implies that a subsonic flow of a gas ($M < 1$) moving upward ($dz > 0$) is accelerated ($dw > 0$) and a supersonic flow ($M > 1$) moving upward is decelerated. These conclusions are of interest when we analyze the processes of natural gas discharge from a well (whose section is constant along the height).

If $\Sigma$ is constant and $q_{\text{ext}} = 0$, $l_{\text{tech}} = 0$, and $z = \text{const}$ and there is energy dissipation due to friction in the flow, Eq. (5.226) is transformed to

$$(M^2 - 1)\frac{dw}{w} = -\left(\frac{\alpha}{c_p} + \frac{1}{a^2}\right) dl_{\text{diss}}. \tag{5.230}$$

We note that unlike the differentials $d\Sigma$, $dq_{\text{ext}}$, $dl_{\text{tech}}$, and $dz$ in Eq. (5.226), which can be both positive and negative, the work of overcoming frictional forces can only be positive ($dl_{\text{diss}} > 0$). We see from (5.230) that a subsonic adiabatic flow with friction in a horizontal channel with a constant cross section is accelerated ($dw > 0$). Obviously, such flow can be accelerated to sound velocity, in principle, but cannot exceed it, since we would have to reject heat from the flow and we have already noted that $l_{\text{diss}}$ is always positive, in both subsonic and supersonic flow.

Finally, let us examine the case where $\Sigma$ is constant and $q_{\text{ext}} = 0$, $l_{\text{diss}} = 0$, and $z = \text{const}$, but gas consumption in the channel varies. We can change the consumption $G$ by flowing or suction of the gas through holes in the lateral surface of the channel. For this case ($G$ not constant) from (5.201) it follows that

$$dv = v\left(\frac{d\Sigma}{\Sigma} + \frac{dw}{w} - \frac{dG}{G}\right). \tag{5.231}$$

If we substitute this relation into (5.221) instead of (5.224), we obtain from (5.216) for the case under consideration

$$(M^2 - 1)\frac{dw}{w} = -\frac{dG}{G}. \tag{5.232}$$

This relation implies that the subsonic velocity of the flow ($M < 1$) increases with increasing consumption ($dw > 0$ for $dG > 0$), and the supersonic velocity of the flow ($M > 1$) increases with decreasing consumption ($dw > 0$ for $dG < 0$).

Equations similar to Eq. (5.226) for the flow velocity can also be derived for pressure, temperature, and specific volume of the flow of a fluid.

# 6 The Discontinuities of Thermodynamic Quantities on Boundary Curves

## 6.1 Crossing Boundary Curves: Salient Points and Discontinuities of Thermodynamic Functions

6.1.1. We know that at different values of the external parameters a substance can be in various physical states. These may be the various phases of a substance (i.e. solid, liquid, or gaseous), the various allotropic modifications of a solid substance, the superconducting and normal states of a superconductor, the various states in ferromagnets (ferromagnetic and paramagnetic), antiferromagnets, ferroelectrics (ferroelectric and dielectric), or liquid helium (helium I and helium II).

The curves that separate the domains of different physical states of a substance on the thermodynamic state surface of a substance are called *boundary curves*[1]. Thus on one side of a boundary curve the substance is in one physical state, and on the other it is in another state. Consequently, when a boundary curve is crossed, the properties of the substance change. Experiments have shown that this change is usually of an abrupt discontinuous nature; many thermodynamic quantities undergo a so-called discontinuity of the first kind on the boundary curve.

From thermodynamics we know that the chemical potential of a substance $\varphi$ remains continuous while crossing a boundary curve; the coexisting phases always have equal values of $\varphi$ in addition to temperature and pressure. As for the other thermodynamic quantities, their changes depend on the type of phase transition on the boundary curve: the discontinuities are either in the first derivatives of the chemical potential ($v$ and $s$, for instance) and its higher-order derivatives or only in the second and higher-order derivatives while the first derivatives are continuous (the question of different types of phase transitions is discussed in detail in the following chapter).

Obviously, if a thermodynamic function undergoes a discontinuity of the first kind while crossing the boundary curve, its antideriva-

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[1] In thermodynamics it is customary to designate the lines that separate the region of a two-phase state of a substance from one-state regions as boundary curves (left and right); the other boundary curves (for instance, the line of phase transition in a $p$, $T$-diagram) are usually called *curves* (or *lines*) *of phase transition*. Naturally, this is not a matter of principle and in the future we will use exclusively the term boundary curve.

tive at the point of transition through the boundary curve has a salient point. For example, an isentrope in the $p$, $v$-diagram has a salient point where it intersects a boundary curve, while in the $(\partial p/\partial v)_s$, $v$-diagram an isentrope has a discontinuity of the first kind at this point (see Fig. 6.1, where (*a*) is a $p$, $v$-diagram and (*b*) a $(\partial p/\partial v)_s$, $v$-diagram).

6.1.2. We see that on the thermodynamic state surface of a given substance each boundary curve is uniquely fixed. But if the line is fixed on the state surface, any thermodynamic quantity at each point of this line is a function of only one variable. This can be demonstrated by a simple example. Figure 6.2 shows a line in the $x$, $y$, $z$ space belonging to the surface $z$ $(x, y)$. If the value of one variable is fixed (for instance, $y = y_0$), then, as is clear from Fig. 6.2, there is a point on this line, $a$, uniquely fixed by the other two coordinates ($x = x_0$ and $y = y_0$). We see that each of the two variables ($x$ and $y$, $x$ and $z$, $y$ and $z$) is uniquely related to the other. For instance, let us examine in $p$, $v$, $T$-coordinates the right boundary curve separating the region of gaseous state of a substance from the two-phase, liquid-vapor, region. If the temperature $T$ is given, the values of pressure $p$ and specific volume $v''$ are uniquely specified at a given point on the boundary curve; if $p$ is given, $T$ and $v''$ are uniquely specified; and if $v''$ is given, $p$ and $T$ are uniquely specified.

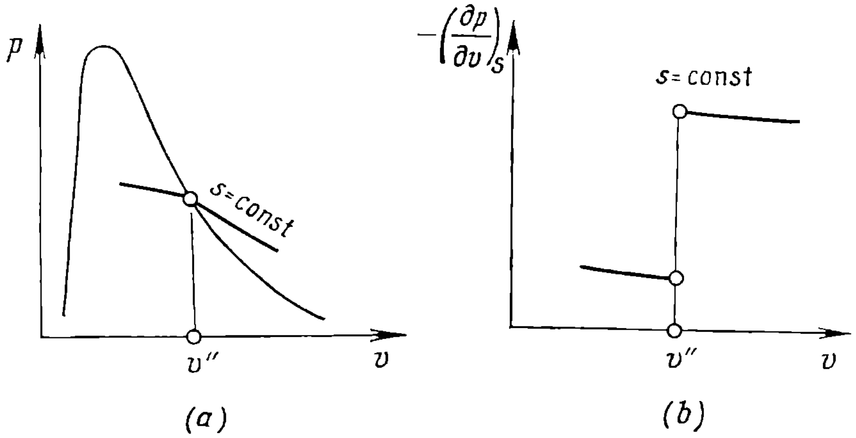

Fig. 6.1

If we take the projection of this line on any of the three coordinate planes, we see that since a thermodynamic quantity on this projection is, naturally, a function of one variable, its derivative with respect to this variable is total (and not partial). Thus, in the $v$, $T$ plane the derivative of $v''$ with respect to $T$ is the total derivative $dv''/dT$, in the $v$, $p$ plane the derivative of $v''$ with respect to $p$ is the total derivative $dv''/dp$, and in the $p$, $T$ plane the derivative of $p$ with respect to $T$ is the total derivative $dp/dT$.

We can write these derivatives as partial, but then we must bear in mind that the derivatives are taken along the right boundary curve:

$$\frac{dv''}{dT}=\left(\frac{\partial v}{\partial T}\right)_{\substack{\text{right}\\ \text{boundary}\\ \text{curve}}},\quad \frac{dv''}{dp}=\left(\frac{\partial v}{\partial p}\right)_{\substack{\text{right}\\ \text{boundary}\\ \text{curve}}},\quad \frac{dp}{dT}=\left(\frac{\partial p}{\partial T}\right)_{\substack{\text{boundary}\\ \text{curve}}}. \tag{6.1}$$

Sometimes we can see such notation in the literature.

6.1.3. It is interesting to obtain differential equations that determine the value of the discontinuity of a function crossing the boundary curve. The general method of obtaining such relations is as follows.

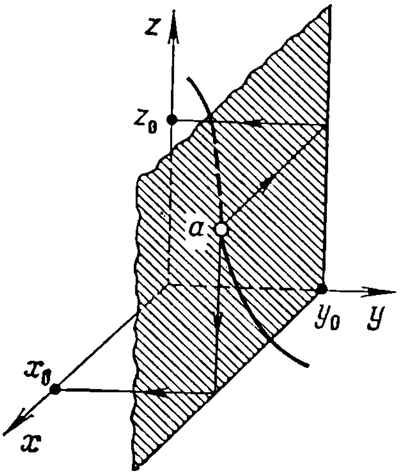

Fig. 6.2

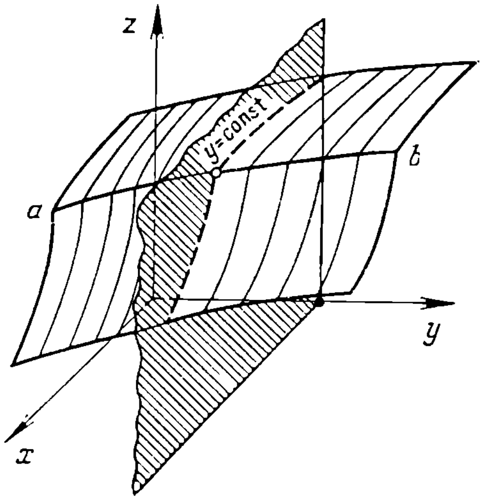

Fig. 6.3

Let us examine Fig. 6.3. Here *a-b* is a boundary curve on the thermodynamic state surface. The line $y$ = const formed where the surface intersects the plane $y$ = const, has a salient point at $m$. Hence, the derivative $(\partial z/\partial x)_y$ changes abruptly at this point. Obviously (intersect the surface by the planes $x$ = const and $z$ = const), the derivatives $(\partial z/\partial y)_x$ and $(\partial y/\partial x)_z$ change in a similar manner at this point.

Equation (2.24) for the total differential of the function $z(x, y)$,

$$dz=\left(\frac{\partial z}{\partial x}\right)_y dx+\left(\frac{\partial z}{\partial y}\right)_x dy,$$

implies that if the function changes along the curve *a-b*, its differential can be calculated in two equivalent ways: we can take the partial derivatives in (2.24) either on one side of the boundary curve *a-b* or on the other (in Fig. 6.3 from either above the curve or below it).

If we indicate the partial derivatives taken on one side of the boundary curve by the superscript (1) and the partial derivatives taken on the other side by (2), we can write (2.24) thus

$$dz = \left(\frac{\partial z}{\partial x}\right)_y^{(1)} dx + \left(\frac{\partial z}{\partial y}\right)_x^{(1)} dy \tag{6.2}$$

or thus

$$dz = \left(\frac{\partial z}{\partial x}\right)_y^{(2)} dx + \left(\frac{\partial z}{\partial y}\right)_x^{(2)} dy. \tag{6.3}$$

Hence, we can write a relation for the total derivative $dz/dx$ in the form

$$\frac{dz}{dx} = \left(\frac{\partial z}{\partial x}\right)_y^{(1)} + \left(\frac{\partial z}{\partial y}\right)_x^{(1)} \frac{dy}{dx} \tag{6.4}$$

or in the form

$$\frac{dz}{dx} = \left(\frac{\partial z}{\partial x}\right)_y^{(2)} + \left(\frac{\partial z}{\partial y}\right)_x^{(2)} \frac{dy}{dx}. \tag{6.5}$$

Here $(\partial z/\partial x)_y^{(1)}$ and $(\partial z/\partial x)_y^2$ are the partial derivatives taken at the point of intersection of the line $y$ = const with the boundary curve, the first of them taken on one side of the curve and the second on the other (Fig. 6.4*a*); $(\partial z/\partial y)_x^1$ and $(\partial z/\partial y)_x^2$ are the partial derivatives taken at the point of intersection of the line $x$ = const with the boundary curve on one or the other side of the curve (Fig. 6.4*b*); $dy/dx$ is the total derivative of the function $y(x)$ along the boundary curve (Fig. 6.4*c*).

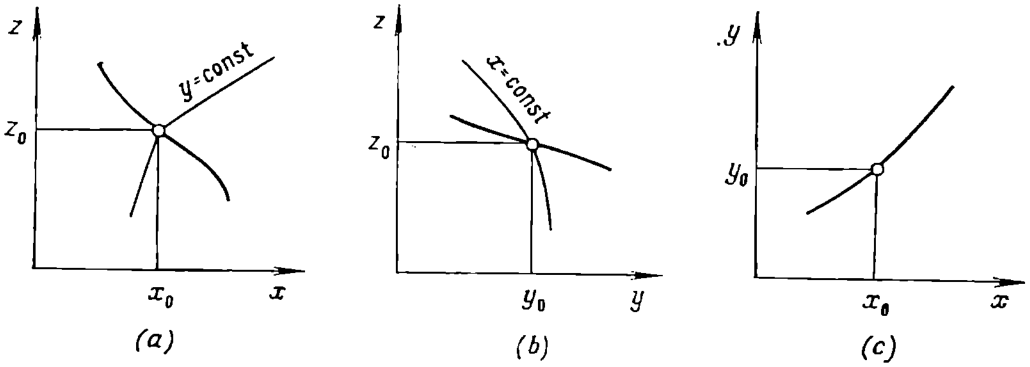

Fig. 6.4

We note once more that the result of calculating the derivative is independent of which of the two absolutely equivalent relations (6.4) or (6.5) we choose.

If we equate the right-hand sides of these relations, we obtain

$$\left(\frac{\partial z}{\partial x}\right)_y^{(1)} + \left(\frac{\partial z}{\partial y}\right)_x^{(1)} \frac{dy}{dx} = \left(\frac{\partial z}{\partial x}\right)_y^{(2)} + \left(\frac{\partial z}{\partial y}\right)_x^{(2)} \frac{dy}{dx}, \qquad (6.6)$$

whence

$$\left(\frac{\partial z}{\partial x}\right)_y^{(1)} - \left(\frac{\partial z}{\partial x}\right)_y^{(2)} = -\left[\left(\frac{\partial z}{\partial y}\right)_x^{(1)} - \left(\frac{\partial z}{\partial y}\right)_x^{(2)}\right] \frac{\partial y}{\partial x}. \qquad (6.7)$$

This relation determines the value of discontinuity of the derivative $(\partial z/\partial x)_y$ crossing the boundary curve. It enables us to calculate the value of the discontinuity of any thermodynamic function with a discontinuity on a boundary curve.

## 6.2 Discontinuity Equations for Thermodynamic Functions on Boundary Curves

6.2.1. Instead of $z$, $x$ and $y$ we can take another set of thermodynamic quantities in Eq. (6.7). For instance, if we assume $z = s$, $x = T$ and $y = p$, then from (6.7) we obtain an equation for the value of discontinuity in the isobaric heat capacity $c_p$ on a boundary curve; if we take $z = T$, $x = p$, and $y = h$, then we can calculate the discontinuity in the Joule-Thomson coefficient on the boundary curve; if $z = \varphi$, $x = T$, and $y = p$, then (6.7) yields an important equation relating the values of discontinuities in $s$ and $v$; and so on.

The analysis of Eq. (6.7) is of the greatest practical interest for the cases where $x$, $y$, and $z$ are replaced by specific entropy $s$, specific volume $v$, temperature $T$, and pressure $p$.

We can easily see that $x$, $y$ and $z$ may be chosen from $s$, $v$, $T$, and $p$ by 12 different ways listed in Table 6.1.

TABLE 6.1

| $z$ | $x$ | $y$ | $z$ | $x$ | $y$ | $z$ | $x$ | $y$ | $z$ | $x$ | $y$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $s$ | $T$ | $p$ | $T$ | $p$ | $v$ | $v$ | $T$ | $p$ | $p$ | $T$ | $v$ |
| $s$ | $T$ | $v$ | $T$ | $p$ | $s$ | $v$ | $T$ | $s$ | $p$ | $T$ | $s$ |
| $s$ | $p$ | $v$ | $T$ | $v$ | $s$ | $v$ | $p$ | $s$ | $p$ | $v$ | $s$ |

It may seem that the number of possible ways is twice that given in Table 6.1, since, for instance, together with $z = s$, $x = T$, $y = p$ the variant $z = s$, $x = p$, $y = T$ is also possible. The point is that because Eq. (6.7) is symmetric in $x$ and $y$, we obtain the same result by a simple interchange of $x$ and $y$.

6.2.2. Let us see what relations we can derive from Eq. (6.7) for each of the variants given in Table 6.1.

We introduce the following notations for the discontinuities of the derivatives $(\partial z/\partial x)_y$ and $(\partial z/\partial y)_x$:

$$\Delta\left(\frac{\partial z}{\partial x}\right)_y=\left(\frac{\partial z}{\partial x}\right)_y^{(1)}-\left(\frac{\partial z}{\partial x}\right)_y^{(2)} \tag{6.8}$$

and

$$\Delta\left(\frac{\partial z}{\partial y}\right)_x=\left(\frac{\partial z}{\partial y}\right)_x^{(1)}-\left(\frac{\partial z}{\partial y}\right)_x^{(2)}. \tag{6.9}$$

(1) $z = s$, $x = T$, $y = p$. Equation (6.7) then assumes the following form:

$$\Delta\left(\frac{\partial s}{\partial T}\right)_p=-\Delta\left(\frac{\partial s}{\partial p}\right)_T\frac{dp}{dT}. \tag{6.10}$$

Since according to (5.100a)

$$\left(\frac{\partial s}{\partial T}\right)_p=\frac{c_p}{T}$$

and according to (4.4)

$$\left(\frac{\partial s}{\partial p}\right)_T=-\left(\frac{\partial v}{\partial T}\right)_p,$$

Eq. (6.10) transforms to

$$\Delta c_p=T\Delta\left(\frac{\partial v}{\partial T}\right)_p\frac{dp}{dT}. \tag{6.11}$$

(2) $z = s$, $x = T$, $y = v$. Here from (6.7) we obtain

$$\Delta\left(\frac{\partial s}{\partial T}\right)_v=-\Delta\left(\frac{\partial s}{\partial v}\right)_T\frac{dv}{dT}. \tag{6.12}$$

Bearing in mind that according to (5.101a)

$$\left(\frac{\partial s}{\partial T}\right)_v=\frac{c_v}{T}$$

and according to (4.3)

$$\left(\frac{\partial s}{\partial v}\right)_T=\left(\frac{\partial p}{\partial T}\right)_v,$$

from (6.12) we obtain

$$\Delta c_v=-T\Delta\left(\frac{\partial p}{\partial T}\right)_v\frac{dv}{dT}. \tag{6.13}$$

(3) $z = s$, $x = p$, $y = v$. Equation (6.7) transforms to

$$\Delta\left(\frac{\partial s}{\partial p}\right)_T=-\Delta\left(\frac{\partial s}{\partial v}\right)_p\frac{dv}{dp}. \tag{6.14}$$

Since according to (4.1a)

$$\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_s$$

and according to (4.2a)

$$\left(\frac{\partial s}{\partial v}\right)_p = \left(\frac{\partial p}{\partial T}\right)_s,$$

from (6.14) it follows that

$$\Delta\left(\frac{\partial v}{\partial T}\right)_s = \Delta\left(\frac{\partial p}{\partial T}\right)_s \frac{dv}{dp}. \tag{6.15}$$

(4) $z = v$, $x = T$, $y = p$. Here Eq. (6.7) assumes the form

$$\Delta\left(\frac{\partial v}{\partial T}\right)_p = -\Delta\left(\frac{\partial v}{\partial p}\right)_T \frac{dp}{dT}. \tag{6.16}$$

(5) $z = v$, $x = T$, $y = s$. From (6.7) we obtain

$$\Delta\left(\frac{\partial v}{\partial T}\right)_s = -\Delta\left(\frac{\partial v}{\partial s}\right)_T \frac{ds}{dT}. \tag{6.17}$$

Since according to (4.3a)

$$\left(\frac{\partial v}{\partial s}\right)_T = \left(\frac{\partial T}{\partial p}\right)_v,$$

from (6.17) it follows that

$$\Delta\left(\frac{\partial v}{\partial T}\right)_s = -\Delta\left(\frac{\partial T}{\partial p}\right)_v \frac{ds}{dT}. \tag{6.18}$$

(6) $z = v$, $x = p$, $y = s$. Equation (6.7) transforms to

$$\Delta\left(\frac{\partial v}{\partial p}\right)_s = -\Delta\left(\frac{\partial v}{\partial s}\right)_p \frac{ds}{dp}. \tag{6.19}$$

Bearing in mind that in accordance with (4.2)

$$\left(\frac{\partial v}{\partial s}\right)_p = \left(\frac{\partial T}{\partial p}\right)_s,$$

from (6.19) we obtain

$$\Delta\left(\frac{\partial v}{\partial p}\right)_s = -\Delta\left(\frac{\partial T}{\partial p}\right)_s \frac{ds}{dp}. \tag{6.20}$$

(7) $z = T$, $x = p$, $y = v$. Here Eq. (6.7) assumes the following form:

$$\Delta\left(\frac{\partial T}{\partial p}\right)_v = -\Delta\left(\frac{\partial T}{\partial v}\right)_p \frac{dv}{dp}. \tag{6.21}$$

(8) $z = T$, $x = p$, $y = s$. From Eq. (6.7) we obtain

$$\Delta\left(\frac{\partial T}{\partial p}\right)_s = -\Delta\left(\frac{\partial T}{\partial s}\right)_p \frac{ds}{dp}. \tag{6.22}$$

Since, as it follows from (5.100a),

$$\left(\frac{\partial T}{\partial s}\right)_p = \frac{T}{c_p},$$

we can transform (6.22) to

$$\Delta\left(\frac{\partial T}{\partial p}\right)_s = -T\Delta\left(\frac{1}{c_p}\right)\frac{ds}{dp}. \tag{6.23}$$

(9) $z = T$, $x = v$, $y = s$. Here Eq. (6.7) transforms to

$$\Delta\left(\frac{\partial T}{\partial v}\right)_s = -\Delta\left(\frac{\partial T}{\partial s}\right)_v\frac{ds}{dv}. \tag{6.24}$$

Since, as we see from (5.101a),

$$\left(\frac{\partial T}{\partial s}\right)_v = \frac{T}{c_v},$$

from (6.24) it follows that

$$\Delta\left(\frac{\partial T}{\partial v}\right)_s = -T\Delta\left(\frac{1}{c_v}\right)\frac{ds}{dv}. \tag{6.25}$$

(10) $z = p$, $x = T$, $y = v$. Here (6.7) assumes the following form:

$$\Delta\left(\frac{\partial p}{\partial T}\right)_v = -\Delta\left(\frac{\partial p}{\partial v}\right)_T\frac{dv}{dT}. \tag{6.26}$$

(11) $z = p$, $x = T$, $y = s$. From Eq. (6.7) we obtain

$$\Delta\left(\frac{\partial p}{\partial T}\right)_s = -\Delta\left(\frac{\partial p}{\partial s}\right)_T\frac{ds}{dT}. \tag{6.27}$$

Since according to (4.4a)

$$\left(\frac{\partial p}{\partial s}\right)_T = -\left(\frac{\partial T}{\partial v}\right)_p,$$

from (6.27) we have

$$\Delta\left(\frac{\partial p}{\partial T}\right)_s = \Delta\left(\frac{\partial T}{\partial v}\right)_p\frac{ds}{dT}. \tag{6.28}$$

(12) $z = p$, $x = v$, $y = s$. Here Eq. (6.7) assumes the form

$$\Delta\left(\frac{\partial p}{\partial v}\right)_s = -\Delta\left(\frac{\partial p}{\partial s}\right)_v\frac{ds}{dv}. \tag{6.29}$$

Bearing in mind that according to (4.1)

$$\left(\frac{\partial p}{\partial s}\right)_v = -\left(\frac{\partial T}{\partial v}\right)_s,$$

from (6.29) we obtain

$$\Delta\left(\frac{\partial p}{\partial v}\right)_s = \Delta\left(\frac{\partial T}{\partial v}\right)_s\frac{ds}{\partial v}. \tag{6.30}$$

We have 12 equations that determine the discontinuities in the derivatives of thermodynamic quantities; namely, the derivatives containing $s$, $v$, $T$, and $p$. Many of these equations are widely used in thermodynamics, and some we will use in the next chapter.

6.2.3. If we examine the above equations for discontinuities of thermodynamic quantities on boundary curves, we can see that the equations containing the same values of total derivatives of thermodynamic quantities along the boundary curve can be in pairs. For instance, both Eq. (6.11) and Eq. (6.16) contain $dp/dT$, Eqs. (6.13) and (6.26) contain $dv/dT$, and so on. Grouping the equations in pairs according to this criterion and excluding the same total derivatives, we obtain a new set of useful equations.

If we write Eq. (6.11) as

$$\frac{dp}{dT}=\frac{\Delta c_p}{T\Delta\left(\frac{\partial v}{\partial T}\right)_p}, \tag{6.31}$$

and Eq. (6.16) as

$$\frac{dp}{dT}=-\frac{\Delta\left(\frac{\partial v}{\partial T}\right)_p}{\Delta\left(\frac{\partial v}{\partial p}\right)_T} \tag{6.32}$$

and equate the right-hand sides of these equations, we obtain

$$\Delta c_p=-T\frac{\left[\Delta\left(\frac{\partial v}{\partial T}\right)_p\right]^2}{\Delta\left(\frac{\partial v}{\partial p}\right)_T}. \tag{6.33}$$

In a similar manner, if we exclude $dv/dT$ from (6.13) and (6.26), we obtain

$$\Delta c_v=T\frac{\left[\Delta\left(\frac{\partial p}{\partial T}\right)_v\right]^2}{\Delta\left(\frac{\partial p}{\partial v}\right)_T}. \tag{6.34}$$

Excluding the total derivative $ds/dp$ from (6.20) and (6.23), we have

$$\Delta\left(\frac{1}{c_p}\right)=\frac{\left[\Delta\left(\frac{\partial T}{\partial p}\right)_s\right]^2}{T\Delta\left(\frac{\partial v}{\partial p}\right)_s}. \tag{6.35}$$

If we exclude $ds/dv$ from (6.25) and (6.30), we find that

$$\Delta\left(\frac{1}{c_v}\right)=-\frac{\left[\Delta\left(\frac{\partial T}{\partial v}\right)_s\right]^2}{T\Delta\left(\frac{\partial p}{\partial v}\right)_s}. \tag{6.36}$$

Excluding $dv/dp$ from (6.15) and (6.21), we obtain

$$\Delta\left(\frac{\partial v}{\partial T}\right)_s \Delta\left(\frac{\partial T}{\partial v}\right)_p = -\Delta\left(\frac{\partial T}{\partial p}\right)_v \Delta\left(\frac{\partial p}{\partial T}\right)_s. \tag{6.37}$$

Finally, if we exclude $ds/dT$ from (6.18) and (6.28), we obtain an equation that coincides with (6.37).

Equations (6.33) through (6.37) relate the values of discontinuities of different thermodynamic quantities on the boundary curve.

6.2.4. Equations (6.10) through (6.30) can easily be grouped in pairs according to another criterion, namely, by the values of discontinuities of the same thermodynamic quantities. For instance, both Eqs. (6.11) and (6.16) contain $\Delta\,(\partial v/\partial T)_p$, Eqs. (6.13) and (6.26) contain $\Delta\,(\partial p/\partial T)_v$, and so on. Grouping the equations in pairs and excluding the same values of discontinuities, we obtain another set of useful equations.

If we exclude $\Delta\,(\partial v/\partial T)_p$ from (6.11) and (6.16), we obtain

$$\Delta c_p = -T\Delta\left(\frac{\partial v}{\partial p}\right)_T \left(\frac{dp}{dT}\right)^2. \tag{6.38}$$

If we exclude $\Delta\,(\partial p/\partial T)_v$ from (6.13) and (6.26), we obtain

$$\Delta c_v = T\Delta\left(\frac{\partial p}{\partial v}\right)_T \left(\frac{dv}{dT}\right)^2. \tag{6.39}$$

If we exclude $\Delta\,(\partial T/\partial p)_s$ from (6.20) and (6.23), we find that

$$\Delta\left(\frac{1}{c_p}\right) = \frac{1}{T}\Delta\left(\frac{\partial v}{\partial p}\right)_s \left(\frac{dp}{ds}\right)^2, \tag{6.40}$$

while if we exclude $\Delta\,(\partial T/\partial v)_s$ from (6.25) and (6.30), we have

$$\Delta\left(\frac{1}{c_v}\right) = -\frac{1}{T}\Delta\left(\frac{\partial p}{\partial v}\right)_s \left(\frac{dv}{ds}\right)^2. \tag{6.41}$$

Excluding $\Delta\,(\partial v/\partial T)_s$ from (6.15) and (6.18), we obtain

$$\Delta\left(\frac{\partial p}{\partial T}\right)_s \frac{dv}{dp} = -\Delta\left(\frac{\partial T}{\partial p}\right)_v \frac{ds}{dp}, \tag{6.42}$$

and excluding $\Delta\,(\partial T/\partial v)_p$ from (6.21) and (6.28), we obtain the same relation.

Similarly, if we exclude $\Delta\,(\partial p/\partial T)_s$ from (6.15) and (6.28), we obtain

$$\Delta\left(\frac{\partial v}{\partial T}\right)_s \frac{dp}{dv} = \Delta\left(\frac{\partial T}{\partial v}\right)_s \frac{ds}{dT}, \tag{6.43}$$

while if we exclude $\Delta\,(\partial T/\partial p)_v$ from (6.18) and (6.21), we obtain the same relation.

Equations (6.38) through (6.43) complete the group of basic equations relating the values of discontinuities of different thermodynamic quantities crossing boundary curves and total derivatives of the thermodynamic quantities along these boundary curves.

6.2.5. We know that if we consider a thermodynamic system with $\xi$ a generalized force and $w$ a generalized coordinate, then the equations obtained above can be written in the following form.

The first group of relations is

$$\Delta c_\xi = T\Delta\left(\frac{\partial w}{\partial T}\right)_\xi \frac{d\xi}{dT}, \tag{6.44}$$

$$\Delta c_w = -T\Delta\left(\frac{\partial \xi}{\partial T}\right)_w \frac{dw}{dT}, \tag{6.45}$$

$$\Delta\left(\frac{\partial w}{\partial T}\right)_s = \Delta\left(\frac{\partial \xi}{\partial T}\right)_s \frac{dw}{dp}, \tag{6.46}$$

$$\Delta\left(\frac{\partial w}{\partial T}\right)_\xi = -\Delta\left(\frac{\partial w}{\partial \xi}\right) \frac{d\xi}{dT}, \tag{6.47}$$

$$\Delta\left(\frac{\partial w}{\partial T}\right)_s = -\Delta\left(\frac{\partial T}{\partial \xi}\right)_w \frac{ds}{dT}, \tag{6.48}$$

$$\Delta\left(\frac{\partial w}{\partial \xi}\right)_s = -\Delta\left(\frac{\partial T}{\partial \xi}\right)_s \frac{ds}{d\xi}, \tag{6.49}$$

$$\Delta\left(\frac{\partial T}{\partial \xi}\right)_w = -\Delta\left(\frac{\partial T}{\partial w}\right)_\xi \frac{dw}{d\xi}, \tag{6.50}$$

$$\Delta\left(\frac{\partial T}{\partial \xi}\right)_s = -T\Delta\left(\frac{1}{c_\xi}\right) \frac{ds}{d\xi}, \tag{6.51}$$

$$\Delta\left(\frac{\partial T}{\partial w}\right)_s = -T\Delta\left(\frac{1}{c_w}\right) \frac{ds}{dw}, \tag{6.52}$$

$$\Delta\left(\frac{\partial \xi}{\partial T}\right)_w = -\Delta\left(\frac{\partial \xi}{\partial w}\right)_T \frac{dw}{dT}, \tag{6.53}$$

$$\Delta\left(\frac{\partial \xi}{\partial T}\right)_s = \Delta\left(\frac{\partial T}{\partial w}\right)_\xi \frac{ds}{dT}, \tag{6.54}$$

$$\Delta\left(\frac{\partial \xi}{\partial w}\right)_s = \Delta\left(\frac{\partial T}{\partial w}\right)_s \frac{ds}{dw}. \tag{6.55}$$

The second group of relations is

$$\Delta c_\xi = -T\frac{\left[\Delta\left(\frac{\partial w}{\partial T}\right)_\xi\right]^2}{\Delta\left(\frac{\partial w}{\partial \xi}\right)_T}, \tag{6.56}$$

$$\Delta c_w = T\frac{\left[\Delta\left(\frac{\partial \xi}{\partial T}\right)_w\right]^2}{\Delta\left(\frac{\partial \xi}{\partial w}\right)_T}, \tag{6.57}$$

$$\Delta\left(\frac{1}{c_\xi}\right) = \frac{\left[\Delta\left(\frac{\partial T}{\partial \xi}\right)_s\right]^2}{T\Delta\left(\frac{\partial w}{\partial \xi}\right)_s}, \tag{6.58}$$

$$\Delta\left(\frac{1}{c_w}\right)=-\frac{\left[\Delta\left(\frac{\partial T}{\partial w}\right)_s\right]^2}{T\Delta\left(\frac{\partial \xi}{\partial w}\right)_s}, \tag{6.59}$$

$$\Delta\left(\frac{\partial w}{\partial T}\right)_s\Delta\left(\frac{\partial T}{\partial w}\right)_\xi=-\Delta\left(\frac{\partial T}{\partial \xi}\right)_w\Delta\left(\frac{\partial \xi}{\partial T}\right)_s. \tag{6.60}$$

Finally, the third group of relations is

$$\Delta c_\xi=-T\Delta\left(\frac{\partial w}{\partial \xi}\right)_T\left(\frac{d\xi}{dT}\right)^2, \tag{6.61}$$

$$\Delta c_w=T\Delta\left(\frac{\partial \xi}{\partial w}\right)_T\left(\frac{dw}{dT}\right)^2, \tag{6.62}$$

$$\Delta\left(\frac{1}{c_\xi}\right)=\frac{1}{T}\Delta\left(\frac{\partial w}{\partial \xi}\right)_s\left(\frac{d\xi}{ds}\right)^2, \tag{6.63}$$

$$\Delta\left(\frac{1}{c_w}\right)=\frac{1}{T}\Delta\left(\frac{\partial \xi}{\partial w}\right)_s\left(\frac{dw}{ds}\right)^2, \tag{6.64}$$

$$\Delta\left(\frac{\partial \xi}{\partial T}\right)_s\frac{dw}{d\xi}=-\Delta\left(\frac{\partial T}{\partial \xi}\right)_w\frac{ds}{dT}, \tag{6.65}$$

$$\Delta\left(\frac{\partial w}{\partial T}\right)_s\frac{d\xi}{dw}=\Delta\left(\frac{\partial T}{\partial w}\right)_\xi\frac{ds}{dT}. \tag{6.66}$$

These equations give the values of the discontinuities of thermodynamic quantities on the boundary curves of complex systems.

# 7 Phase Transitions

## 7.1 A General Survey

7.1.1. As is known, a phase is a homogeneous region in a heterogeneous system and phase transition is the transfer of matter from one phase to another phase coexisting with the first. Matter can be in a gaseous, liquid, or solid phase; some solid substances have several phases.

A thermodynamic analysis of the conditions of phase equilibrium shows that if two phases are in equilibrium, then the temperature, generalized force, and chemical potential of these must be equal:

$$T_1 = T_2, \tag{7.1}$$

$$\zeta_1 = \zeta_2, \tag{7.2}$$

and

$$\varphi_1 = \varphi_2, \tag{7.3}$$

where the labels 1 and 2 refer to the first and second coexisting phases.

For the particular case of systems performing exclusively work of expansion (below we mainly discuss such systems), condition (7.2) may be written as

$$p_1 = p_2. \tag{7.4}$$

Equations (7.2) and (7.4) imply that if the phase transition occurs at constant pressure, the temperature also remains constant in this process.

We note that conditions (7.2) and (7.4) are met only when the interfacial surface has no special properties that must be taken into account. But if the interfacial surface has such properties (in particular, surface tension), we can write condition (7.4) thus:

$$p_1 = p_2 + p^*, \tag{7.5}$$

where $p^*$ is the additional pressure on the liquid phase caused by surface tension. The value of $p^*$ is determined by the well-known Laplace equation

$$p^* = \sigma\left(\frac{1}{\rho_{\mathrm{I}}} + \frac{1}{\rho_{\mathrm{II}}}\right), \tag{7.6}$$

where $\sigma$ is surface tension, and $\rho_{\mathrm{I}}$ and $\rho_{\mathrm{II}}$ are the main radii of curvature of the interfacial surface. In the case of a plane ($\rho_{\mathrm{I}} = \rho_{\mathrm{II}} = \infty$), $p^*$ vanishes and condition (7.5) coincides with (7.4). In the case of a curvilinear interfacial surface, there appears a pressure difference between the coexisting phases defined by Eq. (7.6).

7.1.2. The region on the thermodynamic state surface (and, consequently, on phase diagrams, which are projections of this surface on the coordinate planes) inside which the substance is in the form of a mixture consisting of two coexisting phases is known as a *two-phase region*. This region is separated from single-phase regions by boundary curves, which connect the initial and terminal points of the phase transition in phase diagrams. For the liquid-vapor phase transition the boundary curve on the side of the liquid is usually called the *left* boundary curve and that on the side of the vapor the *right* boundary curve.

We have already pointed out that since inside the two-phase region an isobar and isotherm coincide, it is clear that

$$\left(\frac{\partial p}{\partial v}\right)_T^{\text{two-ph}} = 0, \tag{7.7}$$

$$\left(\frac{\partial T}{\partial v}\right)_p^{\text{two-ph}} = 0, \tag{7.8}$$

$$\left(\frac{\partial T}{\partial s}\right)_p^{\text{two-ph}} = 0, \tag{7.9}$$

and

$$\left(\frac{\partial p}{\partial s}\right)_T^{\text{two-ph}} = 0. \tag{7.10}$$

Thermodynamic quantities on the boundary curves are functions of only one variable; for instance, the specific volume of a liquid on a boundary curve, $v'$, is uniquely determined by the temperature or pressure of the phase transition.

7.1.3. In the $p$, $T$-diagram the two-phase region is simply a line (see Fig. 7.1); for the case of the liquid-vapor phase transition this line is termed the *saturation line*, or *saturation curve*. The derivative $dp/dT$ is an important thermodynamic quantity, which gives the slope of the phase transition curve in the $p$, $T$-diagram. For the liquid-vapor and solid phase-vapor (sublimation) phase transitions $dp/dT$ is always positive. For the solid phase-liquid phase transition (melting) this value can be positive for one substances and negative for another. The relationship between the second derivatives of

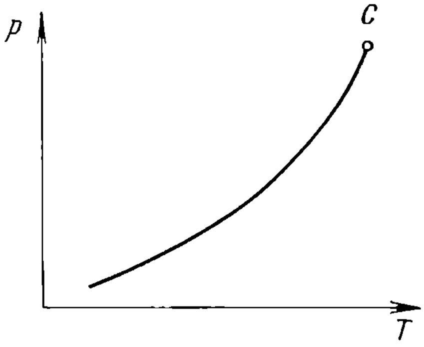

Fig. 7.1

$dp/dT$ with respect to temperature and of $dT/dp$ with respect to pressure is defined (in accordance with (2.17)) by

$$\frac{d^2p}{dT^2} = -\left(\frac{dp}{dT}\right)^3 \frac{d^2T}{dp^2} \tag{7.11}$$

(we will use this relation in the future).

7.1.4. In a phase transition the quantities that are the first derivatives of a thermodynamic potential (namely, specific volume $v$, entropy $s$, internal energy $u$, enthalpy $h$, and free energy $f$) change discontinuously from the value on one boundary curve to that on another. We discuss equations for phase transitions using the notations for the liquid-vapor phase transition. We must bear in mind, however, that these relations, according to their physical meaning, are of a general character and valid for any phase transitions. Let us assume that the prime on a symbol refers to the corresponding quantity on the left boundary curve and two primes to that on the right boundary curve; when a boundary curve is not indicated, the quantity is labeled by a "sigma", $\sigma$.

7.1.5. The quantities that are the first derivatives of a potential are known to be additive inside the two-phase region:

$$v^{\text{two-ph}} = v'(1-x) + v''x, \tag{7.12}$$

$$s^{\text{two-ph}} = s'(1-x) + s''x, \tag{7.13}$$

$$u^{\text{two-ph}} = u'(1-x) + u''x, \tag{7.14}$$

$$h^{\text{two-ph}} = h'(1-x) + h''x, \tag{7.15}$$

$$f^{\text{two-ph}} = f'(1-x) + f''x, \tag{7.16}$$

where $x$ is the so-called *degree of dryness* of a two-phase mixture, which is the ratio of the mass of dry saturated vapor in the mixture to the total mass of the mixture. Equations (7.12) through (7.16) imply that the degree of dryness can be expressed thus:

$$x = \frac{v^{\text{two-ph}} - v'}{v'' - v'} = \frac{s^{\text{two-ph}} - s'}{s'' - s'} = \frac{u^{\text{two-ph}} - u'}{u'' - u'} = \frac{h^{\text{two-ph}} - h'}{h'' - h'} = \frac{f^{\text{two-ph}} - f'}{f'' - f'}. \tag{7.17}$$

7.1.6. Specific quantities associated only with a phase transition curve are: the heat capacity along the boundary curve,

$$c_s = T\frac{ds_\sigma}{dT}, \tag{7.18}$$

where $ds_\sigma/dT$ is the total derivative of entropy with respect to temperature along the boundary curve, and the heat capacity of the two-phase region with the degree of dryness kept constant,

$$c_x = T\left(\frac{\partial s}{\partial T}\right)_x. \tag{7.19}$$

These concepts can be useful in analyzing processes in two-phase systems. Speaking of $c_s$, we note that $ds'/dT$ is always positive and, consequently, $c_s'$ is always positive. But $ds''/dT < 0$, as a rule, and so $c_s'' < 0$.[1]

7.1.7. We note in conclusion that the peculiarities in the thermodynamic properties of the two-phase region result, as we will see from the following sections, in a wide range of interesting and elegant differential equations describing these properties.

## 7.2 The Clausius-Clapeyron Equation and Its Analogs

7.2.1. As we have noted, coexisting phases have equal chemical potentials $\varphi$, but the specific entropy $s$ and the specific volume $v$ of the substance in a phase transition change abruptly. It is interesting to obtain a relation that connects the values of the discontinuities in $s$ and $v$ in phase transition.

To do this, we use the general equation (6.7) for the values of the discontinuities in a transition across a boundary curve,

$$\left(\frac{\partial z}{\partial x}\right)_y^{(1)} - \left(\frac{\partial z}{\partial x}\right)_y^{(2)} = -\left[\left(\frac{\partial z}{\partial y}\right)_x^{(1)} - \left(\frac{\partial z}{\partial y}\right)_x^{(2)}\right]\frac{dy}{dx}.$$

If we set $z = \varphi$, $x = T$, and $y = p$, we obtain

$$\left(\frac{\partial \varphi}{\partial T}\right)_p^{(1)} - \left(\frac{\partial \varphi}{\partial T}\right)_p^{(2)} = -\left[\left(\frac{\partial \varphi}{\partial p}\right)_T^{(1)} - \left(\frac{\partial \varphi}{\partial p}\right)_T^{2}\right]\frac{dp}{dT}. \tag{7.20}$$

Since (see (3.35a) and (3.36a))

$$\left(\frac{\partial \varphi}{\partial T}\right)_p = -s, \quad \text{and} \quad \left(\frac{\partial \varphi}{\partial p}\right)_T = v,$$

Eq. (7.20) assumes the form

$$s^{(1)} - s^{(2)} = \left(v^{(1)} - v^{(2)}\right)\frac{dp}{dT}, \tag{7.21}$$

or

$$\frac{dp}{dT} = \frac{s^{(2)} - s^{(1)}}{v^{(2)} - v^{(1)}}, \tag{7.22}$$

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[1] For certain substances (some hydrocarbons, for one) $ds''/dT$ passes through a maximum. Consequently, for such substances $c_s''$ changes its sign at that point on the right boundary curve at which $s''$ attains its maximum.

where $dp/dT$ is the total derivative of the pressure with respect to temperature along the transition curve in the $p$, $T$-diagram, and $s^{(2)}$ and $s^{(1)}$ the entropies at the point of phase transition on the right and left boundary curves.

This equation, which relates the slope of the $p$, $T$ transition curve and the discontinuities in entropy and specific volume at the point of transition, is known as the *Clasius-Clapeyron equation.*

Since, as we have noted in the preceding section, isotherms and isobars coincide in a two-phase region, i.e. at $T$ = const, $p$ is always constant, from (3.28a) written as

$$T\,ds = dh - v\,dp,$$

it follows that here

$$T\,(s^{(2)} - s^{(1)}) = h^{(2)} - h^{(1)}, \tag{7.23}$$

where $h^{(2)}$ and $h^{(1)}$ are the enthalpies of the substance at the point of transition on the right and left boundary curves, respectively. The discontinuity in enthalpy in a phase transition is termed the ***heat of phase transition*** and is usually written as

$$r = h^{(2)} - h^{(1)}. \tag{7.24}$$

Since from (7.23) and (7.24) it follows that

$$s^{(2)} - s^{(1)} = r/T, \tag{7.25}$$

we can write the Clausius-Clapeyron equation as

$$\frac{dp}{dT} = \frac{r}{T\,(v^{(2)} - v^{(1)})}\,. \tag{7.26}$$

The Clausius-Clapeyron equation describes different phase transitions, such as melting, vaporization, and sublimation.

7.2.2. If we examine a phase transition in a thermodynamic system performing work other than work of expansion, i.e. a system in which the generalized force is the parameter $\xi$ and not pressure $p$ and the generalized coordinate is the parameter $w$ and not specific volume $v$, we can obtain an equation similar to the Clausius-Clapeyron equation.

If in Eq. (7.26) we set $z = \varphi^*$, $x = T$, and $y = \xi$, we obtain

$$\left(\frac{\partial\varphi^*}{\partial T}\right)_{\xi}^{(1)} - \left(\frac{\partial\varphi^*}{\partial T}\right)_{\xi}^{(2)} = -\left[\left(\frac{\partial\varphi^*}{\partial\xi}\right)_{T}^{(1)} - \left(\frac{\partial\varphi^*}{\partial\xi}\right)_{T}^{(2)}\right]\frac{d\xi}{dT}\,;$$

taking into account that according to (3.75a)

$$\left(\frac{\partial\varphi^*}{\partial T}\right)_{\xi} = -s$$

and according to (3.77a)

$$\left(\frac{\partial\varphi^*}{\partial\xi}\right)_T = w,$$

we obtain

$$\frac{d\xi}{dT} = \frac{s^{(2)} - s^{(1)}}{w^{(2)} - w^{(1)}}. \tag{7.27}$$

Just as we did with the Clausius-Clapeyron equation, we can write Eq. (7.27) as

$$\frac{d\xi}{dT} = \frac{r}{T\,(w^{(2)} - w^{(1)})}, \tag{7.28}$$

where $d\xi/dT$ is the total derivative of the generalized force $\xi$ with respect to temperature along the transition curve, and $(w^{(2)} - w^{(1)})$ the value of the discontinuity in the generalized coordinate at the point of phase transition. Obviously, for such thermodynamic systems Eqs. (7.27)-(7.28) play the same role as the Clausius-Clapeyron equation for simple systems.

If we want to pass from the general equation (7.27), or (7.28), to the equation for a given system, we must replace $\xi$ and $w$ by the values of generalized force and generalized coordinate for the given system.

Let us consider, for example, the phase transition of a superconductor from the superconducting state to the normal in a magnetic field. We recall that for the thermodynamic system, i.e. a magnetic substance in a magnetic field, the external magnetic field strength $H$ is the generalized force and the magnetization $j$ is the generalized coordinate. Hence, from (7.28) we can see that the analog of the Clausius-Clapeyron equation for such a system is

$$\frac{dH_{\text{cr}}}{dT} = -\frac{q}{T\,(j_{\text{norm}} - j_{\text{super}})}, \tag{7.29}$$

where $dH_{\text{cr}}/dT$ is the slope of the transition curve in the $H$, $T$-diagram ($H_{\text{cr}}$ is the critical magnetic field for a given superconductor), $q$ is the heat of phase transition of the superconductor from the superconducting state to the normal, and $j_{\text{norm}}$ and $j_{\text{super}}$ are the values of specific magnetization in the normal and superconducting phases, respectively.

We know that the (mass) specific magnetization of a superconductor in the superconducting state is given by the formula

$$j_{\text{super}} = -\frac{v_{\text{super}} H_{\text{cr}}}{4\pi}, \tag{7.30}$$

where $v_{\text{super}}$ is the specific volume of a superconductor in the superconducting state. The specific magnetization of a superconductor in the normal state, $j_{\text{norm}}$, is negligible as compared with $j_{\text{super}}$ and we may neglect it in calculating the difference $(j_{\text{norm}} - j_{\text{super}})$. Bearing this in mind, from (7.29) we obtain

$$\frac{dH_{\text{cr}}}{dT} = -\frac{4\pi q}{Tv_{\text{super}}H_{\text{cr}}}. \qquad (7.31)$$

This equation for the phase transition in a superconductor was first obtained by W. Keesom in 1924 and is similar to the Clausius-Clapeyron equation for ordinary systems.

Since the heat of phase transition, $q$, is positive, from (7.31) it follows that always

$$\frac{dH_{\text{cr}}}{dT} < 0, \qquad (7.32)$$

i.e. the critical magnetic field strength of a superconductor increases as the temperature drops. This conclusion corresponds completely to experimental data on the temperature dependence of $H_{\text{cr}}$.

## 7.3. The Phase Transition Equation at Different Pressures in the Phases

7.3.1. For practical applications the cases when the coexisting phases have different pressures are very interesting. One example is the phase equilibrium with a curved interfacial surface; here the pressure difference between the liquid phase and the vapor phase, $p^*$, is given by the Laplace equation (7.6).

Let us now formulate the relation for such phase transitions, similar to the Clausius-Clapeyron equation for ordinary cases.

We note that the required relation, unlike the Clausius-Clapeyron equation, must relate the derivatives $dp_1/dT$ and $dp_2/dT$, where $p_1$ and $p_2$ are the different pressures in the coexisting phases; it is clear that in the general case the variation of $p_1$ and $p_2$ with temperature is not the same (i.e. the derivatives $dp_1/dT$ and $dp_2/dT$ are not equal). This peculiarity does not enable us to use Eq. (6.7) directly, as was done with the Clausius-Clapeyron equation. Nevertheless, we can easily derive the required relation.

Since on the entire transition curve, in accordance with (7.3),

$$\varphi_1 = \varphi_2,$$

the total derivatives $d\varphi/dT$ taken for each of the two phases along the transition curve are equal, too:

$$\frac{d\varphi_1}{dT} = \frac{d\varphi_2}{dT}. \qquad (7.33)$$

Next, from (2.8) it follows that

$$\frac{d\varphi_1}{dT}=\left(\frac{\partial\varphi}{\partial T}\right)_p^{(1)}+\left(\frac{\partial\varphi}{\partial p}\right)_T^{(1)}\frac{\partial p_1}{\partial T} \tag{7.34}$$

and

$$\frac{\partial\varphi_2}{\partial T}=\left(\frac{\partial\varphi}{\partial T}\right)_p^{(2)}+\left(\frac{\partial\varphi}{\partial p}\right)_T^{(2)}\frac{dp_2}{dT}. \tag{7.35}$$

We note once more that the right-hand parts of these relations contain different pressures of the coexisting phases.

If we combine (7.33), (7.34) and (7.35) with (3.36a), (3.35a), and (7.25), we find that

$$v_2\frac{dp_2}{dT}-v_1\frac{dp_1}{dT}=\frac{r}{T}. \tag{7.36}$$

This equation, resembling the Clausius-Clapeyron equation to some extent, relates the quantities *dp*/*dT* for the coexisting phases at different pressures. If the pressures are the same, Eq. (7.36) automatically transforms to the Clausius-Clapeyron equation (7.26).

7.3.2. Now we consider the case where the temperature of the equilibrium phases is kept constant, while the pressure in one of the phases increases. Let us see whether the pressure changes in the other phase, and if it does, what is the law?

Since, obviously (see (2.8)),

$$\frac{dp_2}{dT_1}=\frac{dp_2}{dp_1}\,\frac{dp_1}{dT}, \tag{7.37}$$

we can write Eq. (7.36) as

$$v_2\frac{dp_2}{dp_1}-v_1=\frac{r}{T}\,\frac{dT}{dp_1}. \tag{7.38}$$

If, as we noted above, the temperature in the coexisting phases is kept constant ($dT=0$), from (7.38) it follows that

$$\left(\frac{\partial p_2}{\partial p_1}\right)_T=\frac{v_1}{v_2}. \tag{7.39}$$

This important relation, known as the *Poynting equation*, implies that if the pressure in one of the coexisting phases increases (with $T$ kept constant), the pressure in the second phase increases, too, and the change in pressure in the coexisting phases is inversely proportional to the specific volumes of these phases.

If the two coexisting phases were at the same pressure $p_0$ and then the pressure in one of the phases increased to $p_1$, the increase in pressure in the second phase (from $p_0$ to $p_2$) would be

$$p_2-p_0=\int_{p_0}^{p_1}\left(\frac{\partial p_2}{\partial p_1}\right)_T dp_1, \tag{7.40}$$

whence in accordance with the Poynting equation

$$p_2 - p_0 = \int_{p_0}^{p_1} \frac{v_1}{v_2}\, dp_1. \tag{7.41}$$

If the ratio $v_1/v_2$ does not change considerably with pressure (this is usually the case), we can write (7.41) to an approximation sufficient for practical calculations as[2]

$$p_2 - p_0 = \frac{v_1}{v_2}(p_1 - p_0). \tag{7.42}$$

Next, if we denote the pressure difference between the coexisting phases by

$$p^* = p_1 - p_2, \tag{7.43}$$

from (7.42) it follows that

$$p_1 = p_0 + \frac{v_2}{v_2 - v_1}\, p^*, \tag{7.44}$$

or, which is the same,

$$p_2 = p_0 + \frac{v_1}{v_2 - v_1}\, p^*. \tag{7.45}$$

These equations relate the quantities $p_1$, $p_2$, $p^*$, and $p_0$.

## 7.4. Isolines in a Two-Phase Region in the $p, T$ Plane

7.4.1. Now we consider a particular problem important for the subsequent presentation on the behavior of isolines inside a two-phase region, namely, the isolines $v$ = const, $s$ = const, $u$ = const, $h$ = const, and $f$ = const (we recall that these isolines have a salient point on the boundary curve in the event of a transition from a one-phase region to a two-phase region). In other words, we wish to cal-

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[2] If we are dealing with cases where one of the coexisting phases is the vapor phase, we must not confuse the statement about the weak dependence of the ratio $v_1/v_2$ on $p_1$ with the statement about the strong dependence of $v_2$ (specific volume of the vapor phase) on $p_2$.

From (7.39) we see that if at liquid-vapor equilibrium the pressure in the liquid ($p_1$) increases considerably, the pressure in the vapor phase ($p_2$) changes only slightly, which is due to the great difference between the specific volumes of a liquid and its vapor. Therefore, here $v_2$ changes comparatively little because $p_2$ changes little (though $p_1$ increases considerably) due to the low compressibility of the liquid. We see that in the case of the liquid-vapor (or solid-vapor) equilibrium the ratio $v_1/v_2$ changes only slightly with $p_1$. As for the case of the solid-liquid equilibrium (in which due to the proximity of the values of $v_1$ and $v_2$ the change in pressure in one of the phases results in a commensurable increase in pressure in the other phase), the ratio $v_1/v_2$ changes slightly with an increase in $p_1$ simply because of the low compressibility of both phases.

culate the partial derivatives $(\partial p/\partial T)_v$, $(\partial p/\partial T)_s$, $(\partial p/\partial T)_u$, $(\partial p/\partial T)_h$, and $(\partial p/\partial T)_f$ on the two-phase side of the boundary curves.

The problem is solved in the following way. In accordance with Eq. (6.5), the relation giving the behaviour of the total derivative of pressure with respect to temperature along the saturation line can be written thus:

$$\frac{dp}{dT}=\left(\frac{\partial p}{\partial T}\right)_y^{\text{two-ph}}+\left(\frac{\partial p}{\partial y}\right)_T^{\text{two-ph}}\frac{dy}{dT}. \tag{7.46}$$

Here $(\partial p/\partial T)_y^{\text{two-ph}}$ is the partial derivative taken at the point of intersection of the line $y = \text{const}$ with the boundary curve on the two-phase side of this curve; similarly, $(\partial p/\partial y)_T^{\text{two-ph}}$ is the partial derivative taken at the point of intersection of the isotherm with the boundary curve on the two-phase side of the curve, and $dy/dT$ is the total derivative along the boundary curve. In this equation $y$ can be taken as $v$, $s$, $u$, $h$, $f$, and so on. Let us see how we can transform Eq. (7.46) for different specific values of $y$.

7.4.2. If $y = v$, from (7.46) it follows that

$$\frac{dp}{dT}=\left(\frac{\partial p}{\partial T}\right)_v^{\text{two-ph}}+\left(\frac{\partial p}{\partial v}\right)_T^{\text{two-ph}}\frac{dv_\sigma}{dT}. \tag{7.47}$$

Since on both boundary curves $dv_\sigma/dT$ becomes infinite nowhere except at the critical point, taking into account (7.7), from (7.47) we obtain

$$\frac{dp}{dT}=\left(\frac{\partial p}{\partial T}\right)_v^{\text{two-ph}}. \tag{7.48}$$

Hence, inside the two-phase region on the $p,T$-diagram an isochore coincides with the transition curve.

7.4.3. Assuming $y = s$, from (7.46) we have

$$\frac{dp}{dT}=\left(\frac{\partial p}{\partial T}\right)_s^{\text{two-ph}}+\left(\frac{\partial p}{\partial s}\right)_T^{\text{two-ph}}\frac{ds_\sigma}{dT}. \tag{7.49}$$

Since in accordance with (4.4a)

$$\left(\frac{\partial p}{\partial s}\right)_T=-\left(\frac{\partial T}{\partial v}\right)_p,$$

it follows that

$$\frac{dp}{dT}=\left(\frac{\partial p}{\partial T}\right)_s^{\text{two-ph}}-\left(\frac{\partial T}{\partial v}\right)_p^{\text{two-ph}}\frac{ds_\sigma}{dT}. \tag{7.50}$$

Since $ds_\sigma/dT$ becomes infinite only at the critical point, from (7.8) we find that

$$\frac{dp}{dT}=\left(\frac{\partial p}{\partial T}\right)_s^{\text{two-ph}}, \tag{7.51}$$

i.e. inside the two-phase region on the $p,T$-diagram an isentrope also coincides with the transition curve.

7.4.4. For $y = u$ we can write Eq. (7.46) as

$$\frac{dp}{dT} = \left(\frac{\partial p}{\partial T}\right)_u^{\text{two-ph}} + \left(\frac{\partial p}{\partial u}\right)_T^{\text{two-ph}} \frac{du_\sigma}{dT}. \tag{7.52}$$

Since in accordance with (2.6)

$$\left(\frac{\partial p}{\partial u}\right)_T = \left(\frac{\partial p}{\partial v}\right)_T \left(\frac{\partial v}{\partial u}\right)_T \tag{7.53}$$

and in accordance with (5.2)

$$\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v - p,$$

it follows that, taking into account (7.48), we can transform (7.52) to

$$\frac{dp}{dT} = \left(\frac{\partial p}{\partial T}\right)_u^{\text{two-ph}} + \frac{\left(\frac{\partial p}{\partial v}\right)_T^{\text{two-ph}}}{T\frac{dp}{dT} - p} \frac{du_\sigma}{dT}. \tag{7.54}$$

The quantity $du_\sigma/dT$ on the boundary curve becomes infinite only at the critical point. Hence, taking into account (7.7), we obtain

$$\frac{dp}{dT} = \left(\frac{\partial p}{\partial T}\right)_u^{\text{two-ph}}, \tag{7.55}$$

i.e. inside the two-phase region on the $p,T$-diagram a line $u$ = const coincides with the transition curve.

7.4.5. If we put $y = h$, we can write Eq. (7.46) as

$$\frac{dp}{dT} = \left(\frac{\partial p}{\partial T}\right)_h^{\text{two-ph}} + \left(\frac{\partial p}{\partial h}\right)_T^{\text{two-ph}} \frac{dh_\sigma}{dT}. \tag{7.56}$$

Since in accordance with (5.11)

$$\left(\frac{\partial h}{\partial p}\right)_T = v - T\left(\frac{\partial v}{\partial T}\right)_p,$$

Eq. (7.56) can be transformed to

$$\frac{dp}{dT} = \left(\frac{\partial p}{\partial T}\right)_h^{\text{two-ph}} + \frac{1}{v^{\text{two-ph}} - T\left(\frac{\partial v}{\partial T}\right)_p^{\text{two-ph}}} \frac{dh_\sigma}{dT}. \tag{7.57}$$

The quantity $dh_\sigma/dT$ becomes infinite only at the critical point; at all other points on the boundary curves it has a finite value. Taking this into account and bearing in mind that in accordance with (7.8)

$$\left(\frac{\partial v}{\partial T}\right)_p^{\text{two-ph}} = \infty,$$

from (7.57) we obtain

$$\frac{dp}{dT}=\left(\frac{\partial p}{\partial T}\right)_h^{\text{two-ph}}, \qquad (7.58)$$

i.e. inside the two-phase region on the $p,T$-diagram an isenthalpic curve also coincides with the transition curve.

7.4.6. Finally, if we assume that $y=f$, from (7.46) we have

$$\frac{dp}{dT}=\left(\frac{\partial p}{\partial T}\right)_f^{\text{two-ph}}+\left(\frac{\partial p}{\partial f}\right)_T^{\text{two-ph}}\frac{df_\sigma}{dT}. \qquad (7.59)$$

or, which is the same,

$$\frac{dp}{dT}=\left(\frac{\partial p}{\partial T}\right)_f^{\text{two-ph}}+\frac{1}{\left(\frac{\partial f}{\partial p}\right)_T^{\text{two-ph}}}\frac{df_\sigma}{dT}. \qquad (7.60)$$

Bearing in mind that

$$f=u-Ts,$$

we find that

$$\left(\frac{\partial f}{\partial p}\right)_T=\left(\frac{\partial u}{\partial p}\right)_T-T\left(\frac{\partial s}{\partial p}\right)_T. \qquad (7.61)$$

From (7.53) it follows that

$$\left(\frac{\partial u}{\partial p}\right)_T=\left(\frac{\partial u}{\partial v}\right)_T\left(\frac{\partial v}{\partial p}\right)_T. \qquad (7.62)$$

Hence, if we take into account (5.2), we find that

$$\left(\frac{\partial u}{\partial p}\right)_T=\left[T\left(\frac{\partial p}{\partial T}\right)_v-p\right]\left(\frac{\partial v}{\partial p}\right)_T. \qquad (7.63)$$

In accordance with (4.4),

$$\left(\frac{\partial s}{\partial p}\right)_T=-\left(\frac{\partial v}{\partial T}\right)_p.$$

Substituting (4.4) and (7.63) into (7.61), we obtain

$$\left(\frac{\partial f}{\partial p}\right)_T=\left[T\left(\frac{\partial p}{\partial T}\right)_v-p\right]\left(\frac{\partial v}{\partial p}\right)_T+T\left(\frac{\partial v}{\partial T}\right)_p, \qquad (7.64)$$

whence, after simple transformations and taking into account the fact that

$$\left(\frac{\partial p}{\partial T}\right)_v\left(\frac{\partial v}{\partial p}\right)_T=-\left(\frac{\partial v}{\partial T}\right)_p,$$

we find that

$$\left(\frac{\partial f}{\partial p}\right)_T=-p\left(\frac{\partial v}{\partial p}\right)_T. \qquad (7.65)$$

Then from (7.60) we obtain

$$\frac{dp}{\partial T}=\left(\frac{\partial p}{\partial T}\right)_f^{\text{two-ph}}-\frac{1}{p}\left(\frac{\partial p}{\partial v}\right)_T^{\text{two-ph}}\frac{df_\sigma}{dT}. \tag{7.66}$$

Since the quantity $df_\sigma/dT$ everywhere on the left and right boundary curves (except at the critical point) is finite, from (7.66), with due regard for (7.7), it follows that

$$\frac{dp}{dT}=\left(\frac{\partial p}{\partial T}\right)_f^{\text{two-ph}}, \tag{7.67}$$

i.e. on the $p,T$-diagram a line $f$ = const also coincides with the transition curve inside the two-phase region.

7.4.7. Thus, from (7.48), (7.51), (7.55), (7.58), and (7.67) it follows that

$$\frac{dp}{pT}=\left(\frac{\partial p}{\partial T}\right)_v^{\text{two-ph}}=\left(\frac{\partial p}{\partial T}\right)_s^{\text{two-ph}}=\left(\frac{\partial p}{\partial T}\right)_u^{\text{two-ph}}$$

$$=\left(\frac{\partial p}{\partial T}\right)_h^{\text{two-ph}}=\left(\frac{\partial p}{\partial T}\right)_f^{\text{two-ph}}, \tag{7.68}$$

i.e. all the isolines inside the two-phase region on the $p,T$-diagram coincide with the transition curve. This is not surprising, since if we consider the thermodynamic state surface of a substance in different coordinate systems—in the $p,v,T$ space as well as the $s,T,p$ space the $u,T,p$ space, $h,T,p$ space, and the $f,T,p$ space—we see that the two-phase region is projected onto the $p,T$ plane and becomes the transition curve. It is clear that any lines passing inside the two-phase region in other coordinate planes coincide with this curve.

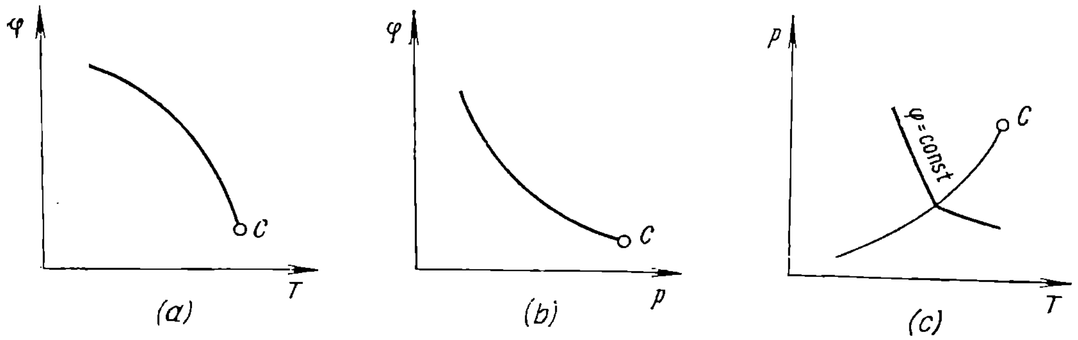

Fig. 7.2

7.4.8. Unlike the quantities $v$, $s$, $u$, $h$ and $f$, which change discontinuously in a phase transition, the chemical potential $\varphi$ for the coexisting phases is the same. Therefore, there is no two-phase region as such on the thermodynamic state surface of a substance in the $\varphi,T,p$ space but only a *line* of the phase transition. Its projection on the $p,T$ coordinate plane will naturally be the same $p,T$ transition curve as in the previous cases. Its projections on the $\varphi, T$ and $\varphi, p$ coordinate planes will also be lines (Fig. 7.2 *a* and *b* shows the $\varphi$ versus $T$ and $\varphi$ versus $p$ curves along the transition line).

We see that a line $\varphi = \text{const}$ on the $p,T$-diagram intersects the transition line. In general the line $\varphi = \text{const}$ has a salient point at the intersection with the transition curve. This results from the following simple reasoning.

It is obvious that

$$\left(\frac{\partial p}{\partial T}\right)_{\varphi} = -\left(\frac{\partial \varphi}{\partial T}\right)_{p} \Big/ \left(\frac{\partial \varphi}{\partial p}\right)_{T}. \tag{7.69}$$

Since in accordance with (3.35a) and (3.36a)

$$\left(\frac{\partial \varphi}{\partial T}\right)_{p} = -s \text{ and } \left(\frac{\partial \varphi}{\partial p}\right)_{T} = v,$$

it follows that

$$\left(\frac{\partial p}{\partial T}\right)_{\varphi} = \frac{s}{v}. \tag{7.70}$$

Hence, at the intersection of the line $\varphi = \text{const}$ with the transition curve on the $p,T$-diagram on the left of the transition curve (in phase 1),

$$\left(\frac{\partial p}{\partial T}\right)_{\varphi}^{(1)} = \frac{s^{(1)}}{v^{(1)}}, \tag{7.71}$$

and on the right of this curve (in phase 2),

$$\left(\frac{\partial p}{\partial T}\right)_{\varphi}^{(2)} = \frac{s^{(2)}}{v^{(2)}}. \tag{7.72}$$

Since in general

$$\frac{s^{(1)}}{s^{(2)}} \neq \frac{v^{(1)}}{v^{(2)}}, \tag{7.73}$$

it is evident that the line $\varphi = \text{const}$ has a salient point at the point under consideration (see Fig. 7.2*c*).

## 7.5 Discontinuity Equations for Thermodynamic Quantities on the Boundary of a Two-Phase Region

7.5.1. As we have noted, the quantities that change abruptly in a phase transition are the first derivatives of a thermodynamic potential, namely, specific volume $v$, entropy $s$, internal energy $u$, enthalpy $h$, and free energy $f$. They change from the values on the left boundary curve to the values on the right boundary curve. But the second derivatives of the potential, such as $c_v$ and $(\partial p/\partial T)_v$, change discontinuously only when we cross the boundary curve. Relations that give the values of these discontinuities are of great practical interest. We can easily obtain them, since they are particular cases of the general discontinuity equations for thermodynamic quantities on the boundary curves obtained in the previous chapter. Let us consider these relations.

7.5.2. We start with the discontinuity of the isochoric heat capacity on a boundary curve. Equation (6.13) combined with (7.48) yields

$$c_v^{\sigma\ \text{two-ph}} - c_v^{\sigma\ \text{one-ph}} = -T\left[\frac{dp}{dT} - \left(\frac{\partial p}{\partial T}\right)_v^{\sigma\ \text{one-ph}}\right]\frac{dv_\sigma}{dT} \qquad (7.74)$$

(superscripts two-ph and one-ph relate to the two-phase and the one-phase side of the boundary curve, while $\sigma$ shows that we are dealing with values on the saturation line).

For the left boundary curve of the liquid-vapor phase transition this equation assumes the form

$$c_v'^{\ \text{two-ph}} - c_v'^{\ \text{one-ph}} = T\left[\left(\frac{\partial p}{\partial T}\right)_v'^{\ \text{one-ph}} - \frac{dp}{dT}\right]\frac{dv'}{dT}, \qquad (7.75)$$

while for the right boundary curve

$$c_v''^{\ \text{two-ph}} - c_v'^{\ \text{two-ph}} = -T\left[\frac{dp}{dT} - \left(\frac{\partial p}{\partial T}\right)_v''^{\ \text{one-ph}}\right]\frac{dv''}{dT}. \qquad (7.76)$$

Since always[3]

$$\left(\frac{\partial p}{\partial T}\right)_v'^{\ \text{one-ph}} > \frac{dp}{dT} \qquad (7.77)$$

and

$$\frac{dv'}{dT} > 0, \qquad (7.78)$$

it follows that always

$$c_v'^{\ \text{two-ph}} - c_v'^{\ \text{one-ph}} > 0. \qquad (7.79)$$

Similarly, since

$$\left(\frac{\partial p}{\partial T}\right)_v''^{\ \text{two-ph}} < \frac{dp}{dT} \qquad (7.80)$$

and

$$\frac{dv''}{dT} < 0, \qquad (7.81)$$

always

$$c_v''^{\ \text{two-ph}} - c_v''^{\ \text{one-ph}} > 0. \qquad (7.82)$$

Thus, the isochoric heat capacity suddenly increases when passing from the one-phase region to the two-phase region. The behavior of

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[3] Except for the critical point (see Chap. 9). In some cases $dv'/dT$ is negative (e.g. for water at $T < 3.98$ °C)

the heat capacity $c_v$ when crossing the boundary curve is shown in Fig. 7.3 (here *I* is the two-phase region and *II* the one-phase region).

(We note once more that this conclusion relates to the liquid-vapor phase transition). The same can be said about sublimation, since for this phase transition $dv_{\text{vap}}/dT < 0$ and $dv_{\text{solid}}/dT > 0$.

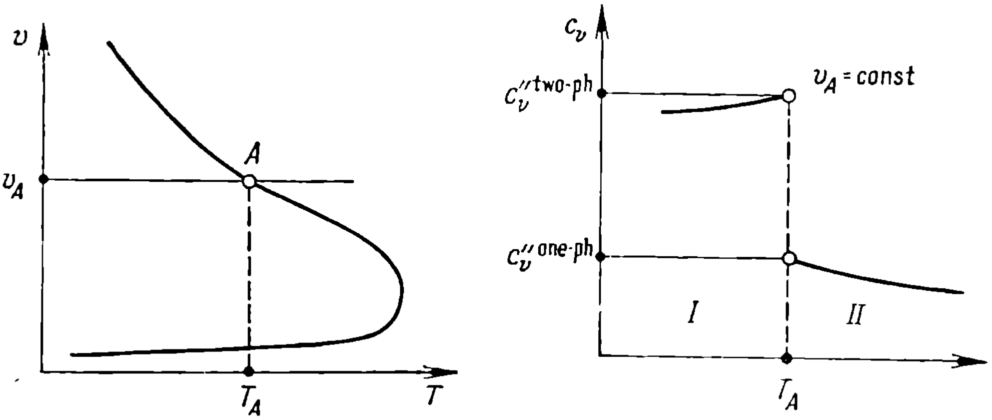

Fig. 7.3

As for melting, $dv_{\text{liq}}/dT$ and $dv_{\text{solid}}/dT$ on the boundary curve are positive for some substances and negative for others.

In the previous chapter we saw that the equations for the discontinuity in the heat capacity $c_v$ when crossing the boundary curve can also be written in the form (6.34)

$$\Delta c_v = T\left[\Delta\left(\frac{\partial p}{\partial T}\right)_v\right]^2 \Big/ \Delta\left(\frac{\partial p}{\partial v}\right)_T$$

or in form (6.39)

$$\Delta c_v = T\Delta\left(\frac{\partial p}{\partial v}\right)_T\left(\frac{dv}{dT}\right)^2.$$

If we combine these equations with (7.48) and (7.7), we obtain for the case under consideration, respectively,

$$c_v'^{\,\text{two-ph}} - c_v'^{\,\text{one-ph}} = -T\left(\frac{\partial v}{\partial p}\right)_T'^{\,\text{one-ph}}\left[\left(\frac{\partial p}{\partial T}\right)_v'^{\,\text{one-ph}} - \frac{dp}{dT}\right]^2 \tag{7.83}$$

and

$$c_v'^{\,\text{two-ph}} - c_v'^{\,\text{one-ph}} = -T\left(\frac{\partial p}{\partial v}\right)_T'^{\,\text{one-ph}}\left(\frac{dv'}{dT}\right)^2 \tag{7.84}$$

and also

$$c_v''^{\,\text{two-ph}} - c_v''^{\,\text{one-ph}} = -T\left(\frac{\partial v}{\partial p}\right)_T''^{\,\text{one-ph}}\left[\frac{dp}{dT} - \left(\frac{\partial p}{\partial T}\right)_v''^{\,\text{one-ph}}\right]^2 \tag{7.85}$$

and

$$c_v''^{\text{ two-ph}} - c_v''^{\text{ one-ph}} = -T\left(\frac{\partial p}{\partial v}\right)_T''^{\text{ one-ph}}\left(\frac{dv''}{dT}\right)^2. \tag{7.86}$$

Knowing the derivatives of thermodynamic quantities on the boundary curve, we can use Eqs. (7.75), (7.76) and (7.83) through (7.86) to calculate with a high degree of accuracy the discontinuity in the heat capacity, $\Delta c_v$, instead of employing a complex calorimetric experiment.

7.5.3. Let us now consider the discontinuities in the adiabatic compressibility, isentropic exponent, and sound velocity on the boundary of the two-phase region. Equation (6.20) for the discontinuity $(\partial v/\partial p)_s$ combined with (7.49) yields

$$\left(\frac{\partial v}{\partial p}\right)_s^{\sigma\text{ two-ph}} - \left(\frac{\partial v}{\partial p}\right)_s^{\sigma\text{ one-ph}} = \left[\frac{dT}{dp} - \left(\frac{\partial T}{\partial p}\right)_s^{\sigma\text{ one-ph}}\right]\frac{ds_\sigma}{dp}. \tag{7.87}$$

For the left boundary curve the equation can be written as

$$\left(\frac{\partial v}{\partial p}\right)_s'^{\text{ two-ph}} - \left(\frac{\partial v}{\partial p}\right)_s'^{\text{ one-ph}} = \left[\frac{dT}{dp} - \left(\frac{\partial T}{\partial p}\right)_s'^{\text{ one-ph}}\right]\frac{ds'}{dp} \tag{7.88}$$

and for the right boundary curve as

$$\left(\frac{\partial v}{\partial p}\right)_s''^{\text{ two-ph}} - \left(\frac{\partial v}{\partial p}\right)_s''^{\text{ one-ph}} = -\left[\left(\frac{\partial T}{\partial p}\right)_s''^{\text{ one-ph}} - \frac{dT}{dp}\right]\frac{ds''}{dp}. \tag{7.89}$$

Equation (6.35)

$$\Delta\left(\frac{1}{c_p}\right) = \frac{\left[\Delta\left(\frac{\partial T}{\partial p}\right)_s\right]^2}{T\Delta\left(\frac{\partial v}{\partial p}\right)_s}$$

combined with Eq. (6.40)

$$\Delta\left(\frac{1}{c_p}\right) = \frac{1}{T}\Delta\left(\frac{\partial v}{\partial p}\right)_s\left(\frac{dp}{ds}\right)^2$$

enables us to write the relations for calculating the discontinuity in $(\partial v/\partial p)_s$ in another form.

If we combine (7.9) with (5.100), we find that

$$c_p^{\text{two-ph}} = \infty. \tag{7.90}$$

Bearing in mind that in accordance with (7.51)

$$\left(\frac{\partial T}{\partial p}\right)_s^{\text{two-ph}}=\frac{dT}{dp},$$

from (6.35) we obtain

$$\left(\frac{\partial v}{\partial p}\right)_s^{\prime\,\text{two-ph}}-\left(\frac{\partial v}{\partial p}\right)_s^{\prime\,\text{one-ph}}=-\frac{c_p^{\prime\,\text{one-ph}}}{T}\left[\frac{dT}{dp}-\left(\frac{\partial T}{\partial p}\right)_s^{\prime\,\text{one-ph}}\right]^2 \tag{7.91}$$

and

$$\left(\frac{\partial v}{\partial p}\right)_s^{\prime\prime\,\text{two-ph}}-\left(\frac{\partial v}{\partial p}\right)_s^{\prime\prime\,\text{one-ph}}=-\frac{c_p^{\prime\prime\,\text{one-ph}}}{T}\left[\left(\frac{\partial T}{\partial p}\right)_s^{\prime\prime\,\text{one-ph}}-\frac{dT}{dp}\right]^2. \tag{7.92}$$

Here $(\partial T/\partial p)_s^{\sigma\,\text{one-ph}}$ is the derivative taken on the isentrope at the point of intersection with the boundary curve on the one-phase side, and $c_p^{\sigma\,\text{one-ph}}$ is the isobaric heat capacity on the boundary curve on the one-phase side.

The quantity $dp/ds$ from Eq. (6.40) can be transformed thus:

$$\frac{dp}{ds}=\frac{dp}{dT}\frac{dT}{ds}. \tag{7.93}$$

Bearing in mind the definition of the heat capacity along a boundary curve (7.18), we obtain

$$\frac{dp}{ds}=\frac{T}{c_s}\frac{dp}{dT}. \tag{7.94}$$

Combining this with (6.40), we find that

$$\left(\frac{\partial v}{\partial p}\right)_s^{\prime\,\text{two-ph}}-\left(\frac{\partial v}{\partial p}\right)_s^{\prime\,\text{one-ph}}=-\frac{c_s^{\prime 2}}{Tc_p^{\prime\,\text{one-ph}}}\left(\frac{dT}{dp}\right)^2 \tag{7.95}$$

and

$$\left(\frac{\partial v}{\partial p}\right)_s^{\prime\prime\,\text{two-ph}}-\left(\frac{\partial v}{\partial p}\right)_s^{\prime\prime\,\text{one-ph}}=-\frac{c_s^{\prime\prime 2}}{Tc_p^{\prime\prime\,\text{one-ph}}}\left(\frac{dT}{dp}\right)^2, \tag{7.96}$$

where $c_s'$ and $c_s''$ are the heat capacities along the saturation line for the left and right boundary curves, respectively.

From these equations we see that always

$$\left(\frac{\partial v}{\partial p}\right)_s^{\prime\,\text{two-ph}}-\left(\frac{\partial v}{\partial p}\right)_s^{\prime\,\text{one-ph}}<0 \tag{7.97}$$

and

$$\left(\frac{\partial v}{\partial p}\right)_s^{\prime\prime\,\text{two-ph}}-\left(\frac{\partial v}{\partial p}\right)_s^{\prime\prime\,\text{one-ph}}<0. \tag{7.98}$$

Since, as we know, $(\partial v/\partial p)_s$ is always negative, these relations imply that the absolute value of the derivative $(\partial v/\partial p)_s$ always increases when crossing the boundary curve from the one-phase region to the two-phase region:

$$\left|\left(\frac{\partial v}{\partial p}\right)_s^{\sigma\ \text{two-ph}}\right| > \left|\left(\frac{\partial v}{\partial p}\right)_s^{\sigma\ \text{one-ph}}\right|. \tag{7.99}$$

Equations (7.88), (7.89), (7.91), and (7.92) and especially (7.95) and (7.96) are useful for calculating the discontinuities in the adiabatic compressibility, isentropic exponent, and sound velocity in the event of a transition across a boundary curve.

We recall that the quantity given by (5.167) is known as the coefficient of adiabatic compressibility

$$\beta_s = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_s.$$

We see that we can easily calculate the discontinuity in $\beta_s$ if we know the relations for calculating the discontinuity in $(\partial v/\partial p)_s$.

Next, we recall that the isentropic exponent is given by (5.181)

$$k = -\frac{v}{p}\left(\frac{\partial p}{\partial v}\right)_s,$$

whence

$$\left(\frac{\partial v}{\partial p}\right)_s = -\frac{v}{kp}. \tag{7.100}$$

Substituting $(\partial v/\partial p)_s$ into (7.95) and (7.96), we obtain, respectively,

$$\frac{1}{k'^{\text{two-ph}}} - \frac{1}{k'^{\text{one-ph}}} = \frac{pc_s'^2}{Tv'c_p'^{\text{one-ph}}}\left(\frac{dT}{dp}\right)^2 \tag{7.101}$$

and

$$\frac{1}{k''^{\text{two-ph}}} - \frac{1}{k''^{\text{one-ph}}} = \frac{pc_s''^2}{Tv''c_p''^{\text{one-ph}}}\left(\frac{dT}{dp}\right)^2. \tag{7.102}$$

This enables us to calculate the discontinuity in the isentropic exponent of a substance when crossing the boundary curves.

These relations, in particular, imply that for both the left and the right boundary curve the isentropic exponent on the one-phase side of the boundary curve, $k^{\sigma\ \text{one-ph}}$, is always greater than that on the two-phase side, $k^{\sigma\ \text{two-ph}}$.

We recall that the sound velocity in a substance, $a$, is related to $(\partial v/\partial p)_s$ via the Laplace equation (5.191)

$$a = \sqrt{-v^2\left(\frac{\partial p}{\partial v}\right)_s},$$

whence

$$\left(\frac{\partial v}{\partial p}\right)_s = -\left(\frac{v}{a}\right)^2. \tag{7.103}$$

Substituting into (7.95) and (7.96), we see

$$\frac{1}{(a'^{\text{two-ph}})^2} - \frac{1}{(a'^{\text{one-ph}})^2} = \frac{c_s'^2}{Tv'^2 c_p'^{\text{one-ph}}}\left(\frac{dT}{dp}\right)^2 \tag{7.104}$$

and

$$\frac{1}{(a''^{\text{two-ph}})^2} - \frac{1}{(a''^{\text{one-ph}})^2} = \frac{c_s''^2}{Tv''^2 c_p''^{\text{one-ph}}}\left(\frac{dT}{dp}\right)^2. \tag{7.105}$$

These equations give the magnitude of the discontinuity in the sound velocity on the boundary of the two-phase region and show, for one, that in a transition from the one-phase region to the two-phase region the sound velocity always decreases, i.e. $a^{\sigma\,\text{one-ph}} > a^{\sigma\,\text{two-ph}}$.

7.5.4. Now let us study the discontinuity in the Joule-Thomson coefficient on the boundary of the two-phase region. In accordance with (5.168), the Joule-Thomson coefficient is defined thus:

$$\mu = \left(\frac{\partial T}{\partial p}\right)_h.$$

The Joule-Thomson coefficient, like the thermodynamic quantities discussed above, changes abruptly when crossing the boundary curve. The value of the discontinuity can be determined by (6.7).

If we set $z = T$, $x = p$, and $y = h$, from (6.7) we obtain

$$\left(\frac{\partial T}{\partial p}\right)_h^{\sigma\,\text{two-ph}} - \left(\frac{\partial T}{\partial p}\right)_h^{\sigma\,\text{one-ph}} = -\left[\left(\frac{\partial T}{\partial h}\right)_p^{\sigma\,\text{two-ph}} - \left(\frac{\partial T}{\partial h}\right)_p^{\sigma\,\text{one-ph}}\right]\frac{dh_\sigma}{dp} \tag{7.106}$$

or, taking into account (5.168) and (5.106),

$$\mu^{\sigma\,\text{two-ph}} - \mu^{\sigma\,\text{one-ph}} = \left(\frac{1}{c_p^{\sigma\,\text{one-ph}}} - \frac{1}{c_p^{\sigma\,\text{two-ph}}}\right)\frac{dh_\sigma}{dp}. \tag{7.107}$$

Since, as we already know, in the two-phase region

$$c_p^{\text{two-ph}} = \infty,$$

it follows that

$$\mu^{\sigma\,\text{two-ph}} - \mu^{\sigma\,\text{one-ph}} = \frac{1}{c_p^{\sigma\,\text{one-ph}}}\frac{dh_\sigma}{dp}. \tag{7.108}$$

This relation gives the discontinuity in the Joule-Thomson coefficient on a boundary curve.

If we combine (5.168) with (7.58), we can see that

$$\mu^{\text{two-ph}} = \frac{dT}{dp}. \tag{7.109}$$

Hence, the values of $\mu$ on the left and right boundary curves on the two-phase side are the same:

$$\mu'^{\text{two-ph}} = \mu''^{\text{two-ph}} = \mu^{\text{two-ph}}. \tag{7.110}$$

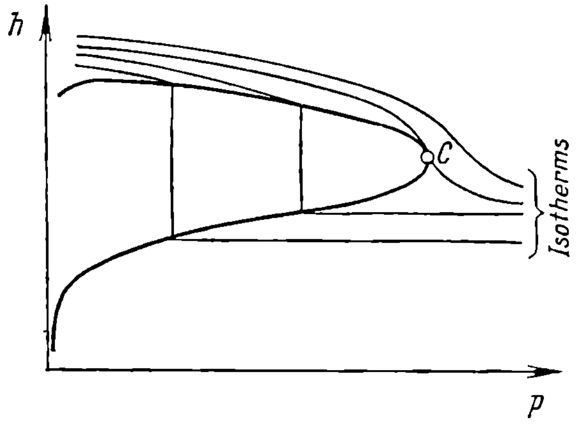

Fig. 7.4

Taking this into account, we can write (7.108) for the left boundary curve as

$$\mu^{\text{two-ph}} - \mu'^{\text{ one-ph}} = \frac{1}{c_p'^{\text{one-ph}}} \frac{dh'}{dp} \tag{7.111}$$

and for the right boundary curve as

$$\mu^{\text{two-ph}} - \mu''^{\text{one-ph}} = \frac{1}{c_p''^{\text{one-ph}}} \frac{dh''}{dp}. \tag{7.112}$$

If we examine the $h,p$-diagram (Fig. 7.4), we see that $dh'/dp$ is always positive, which implies that always

$$\mu'^{\text{one-ph}} < \mu^{\text{two-ph}}. \tag{7.113}$$

From the $h,p$-diagram we also see that in the low pressure regions $dh''/dp$ is positive, and as the pressure increases the sign of the derivative changes. Consequently, at low pressures

$$\mu''^{\text{one-ph}} < \mu^{\text{two-ph}}, \tag{7.114}$$

while at high pressures

$$\mu''^{\text{one-ph}} > \mu^{\text{two-ph}}. \tag{7.115}$$

We see that these inequalities change sign at the point of the saturation line where the enthalpy of dry saturated vapor $h''$ attains the maximum value.

7.5.5. Now let us turn to the equations for the discontinuities in $(\partial p/\partial v)_T$, $(\partial T/\partial v)_p$ and $1/c_p$ on the boundary of the two-phase region. Equations (6.26), (6.21), and (6.23), which describe the transition from the one-phase to the two-phase region, assume the following form:

$$\Delta\left(\frac{\partial p}{\partial v}\right)_T = -\left[\left(\frac{\partial p}{\partial T}\right)_v^{\sigma\ \text{one-ph}} - \frac{dp}{dT}\right]\frac{dT}{dv_\sigma}, \qquad (7.116)$$

$$\Delta\left(\frac{\partial T}{\partial v}\right)_p = -\left[\left(\frac{\partial T}{\partial p}\right)_v^{\sigma\ \text{one-ph}} - \frac{dT}{dp}\right]\frac{dp}{dv_\sigma}, \qquad (7.117)$$

and

$$\Delta\left(\frac{1}{c_p}\right) = -\frac{1}{T}\left[\left(\frac{\partial T}{\partial p}\right)_s^{\sigma\ \text{one-ph}} - \frac{dT}{dp}\right]\frac{dp}{ds_\sigma}, \qquad (7.118)$$

where in accordance with (6.8)

$$\Delta\left(\frac{\partial z}{\partial x}\right)_y = \left(\frac{\partial z}{\partial x}\right)_y^{(1)} - \left(\frac{\partial z}{\partial x}\right)_y^{(2)}.$$

According to (6.4) we can write

$$\frac{dp}{dT} = \left(\frac{\partial p}{\partial T}\right)_v^{\sigma\ \text{one-ph}} + \left(\frac{\partial p}{\partial v}\right)_T^{\sigma\ \text{one-ph}}\frac{dv_\sigma}{dT}, \qquad (7.119)$$

$$\frac{dT}{dp} = \left(\frac{\partial T}{\partial p}\right)_v^{\sigma\ \text{one-ph}} + \left(\frac{\partial T}{\partial v}\right)_p^{\sigma\ \text{one-ph}}\frac{dv_\sigma}{dp}, \qquad (7.120)$$

and

$$\frac{dT}{dp} = \left(\frac{\partial T}{\partial p}\right)_s^{\sigma\ \text{one-ph}} + \left(\frac{\partial T}{\partial s}\right)_p^{\sigma\ \text{one-ph}}\frac{ds_\sigma}{dp}. \qquad (7.121)$$

If we substitute (7.119) into (7.116), (7.120) into (7.117), and (7.121) into (7.118), we obtain, respectively,

$$\Delta\left(\frac{\partial p}{\partial v}\right)_T = \left(\frac{\partial p}{\partial v}\right)_T^{\sigma\ \text{one-ph}}, \qquad (7.122)$$

$$\Delta\left(\frac{\partial T}{\partial v}\right)_p = \left(\frac{\partial T}{\partial v}\right)_p^{\sigma\ \text{one-ph}}, \qquad (7.123)$$

and

$$\Delta\left(\frac{1}{c_p}\right) = \frac{1}{c_p^{\sigma\ \text{one-ph}}}. \qquad (7.124)$$

This result is quite obvious if we consider (7.7), (7.8), and (7.90).

7.5.6. The equations derived in the previous chapter enable us to obtain a few more useful relations determining the discontinuities in thermodynamic quantities on the boundaries of the two-phase region. Relations for the discontinuity in $(\partial v/\partial T)_s$ in the event of a transition across the boundary curve can be obtained in the following way.

First, Eq. (6.15) yields

$$\left(\frac{\partial v}{\partial T}\right)_s^{\sigma\,\text{two-ph}}-\left(\frac{\partial v}{\partial T}\right)_s^{\sigma\,\text{one-ph}}=\left[\frac{dp}{dT}-\left(\frac{\partial p}{\partial T}\right)_s^{\sigma\,\text{one-ph}}\right]\frac{dv_\sigma}{dp}. \tag{7.125}$$

In accordance with (6.4) we can write

$$\frac{dp}{dT}=\left(\frac{\partial p}{\partial T}\right)_s^{\sigma\,\text{one-ph}}+\left(\frac{\partial p}{\partial s}\right)_T^{\sigma\,\text{one-ph}}\frac{ds_\sigma}{dT}. \tag{7.126}$$

Combining this and the Maxwell equation (4.4a), we obtain

$$\left(\frac{\partial v}{\partial T}\right)_s^{\sigma\,\text{two-ph}}-\left(\frac{\partial v}{\partial T}\right)_s^{\sigma\,\text{one-ph}}=-\left(\frac{\partial T}{\partial v}\right)_p^{\sigma\,\text{one-ph}}\frac{c_s}{T}\frac{dv_\sigma}{dp}. \tag{7.127}$$

Second, Eq. (6.18) implies that the same quantities can be written thus:

$$\left(\frac{\partial v}{\partial T}\right)_s^{\sigma\,\text{two-ph}}-\left(\frac{\partial v}{\partial T}\right)_s^{\sigma\,\text{one-ph}}=-\left[\frac{dT}{dp}-\left(\frac{\partial T}{\partial p}\right)_v^{\sigma\,\text{one-ph}}\right]\frac{c_s}{T}. \tag{7.128}$$

If we substitute $dT/dp$ with the help of Eq. (7.120), we arrive at (7.127).

Third, Eq. (6.37) yields

$$\left[\left(\frac{\partial v}{\partial T}\right)_s^{\sigma\,\text{two-ph}}-\left(\frac{\partial v}{\partial T}\right)_s^{\sigma\,\text{one-ph}}\right]\left(\frac{\partial T}{\partial v}\right)_p^{\sigma\,\text{one-ph}}$$
$$=\left[\frac{dT}{dp}-\left(\frac{\partial T}{\partial p}\right)_v^{\sigma\,\text{one-ph}}\right]\left[\frac{dp}{dT}-\left(\frac{\partial p}{\partial T}\right)_s^{\sigma\,\text{one-ph}}\right]. \tag{7.129}$$

If we replace $dT/dp$ with the help of Eq. (7.120) and $dp/dT$ with the help of (7.126), we obtain (7.127).

Finally, Eq. (6.43) also yields (7.127).

We can obtain relations for the discontinuity in $(\partial T/\partial v)_s$ from Eq. (6.25), which for a transition from the two-phase to one-phase region is transformed to

$$\left(\frac{\partial T}{\partial v}\right)_s^{\sigma\,\text{two-ph}}-\left(\frac{\partial T}{\partial v}\right)_s^{\sigma\,\text{one-ph}}=\left(\frac{1}{c_v^{\sigma\,\text{one-ph}}}-\frac{1}{c_v^{\sigma\,\text{two-ph}}}\right)c_s\frac{dT}{dv_\sigma}. \tag{7.130}$$

Relations for the discontinuity in $(\partial p/\partial T)_s$ follow (a) from Eq. (6.23), which we combine with (7.51) and write for the case under consideration

$$\frac{dp}{dT}-\left(\frac{\partial p}{\partial T}\right)_s^{\sigma\,\text{one-ph}}=-\left(\frac{\partial T}{\partial v}\right)_p^{\sigma\,\text{one-ph}}\frac{c_s}{T}, \tag{7.131}$$

and (b) from (6.42)

$$\frac{dp}{dT}-\left(\frac{\partial p}{\partial T}\right)_s^{\sigma\,\text{one-ph}}=-\left[\frac{dT}{dp}-\left(\frac{\partial T}{\partial p}\right)_v^{\sigma\,\text{one-ph}}\right]\frac{c_s}{T}\frac{dp}{dv_\sigma}. \tag{7.132}$$

Transforming (7.132) with the help of (7.120), we can easily show that Eqs. (7.131) and (7.132) are identical.

We can obtain relations for the discontinuity in $(\partial T/\partial p)_s$ from Eq. (6.23) if we bear in mind that in accordance with (7.51)

$$\left(\frac{\partial T}{\partial p}\right)_s^{\text{two-ph}}=\frac{dT}{dp}$$

from (6.23) we obtain

$$\frac{dT}{dp}-\left(\frac{\partial T}{\partial p}\right)_s^{\sigma\,\text{one-ph}}=\frac{T}{c_p^{\sigma\,\text{one-ph}}}\frac{ds_\sigma}{dp}. \tag{7.133}$$

Taking into account that

$$\frac{ds_\sigma}{dp}=\frac{c_s}{T}\frac{dT}{dp}, \tag{7.134}$$

from (7.133) we can obtain an interesting relation

$$\left(\frac{\partial T}{\partial p}\right)_s^{\sigma\,\text{one-ph}}=\left(1-\frac{c_s}{c_p^{\sigma\,\text{one-ph}}}\right)\frac{dT}{dp}. \tag{7.135}$$

From (6.30) we obtain a relation for the discontinuity in $(\partial p/\partial v)_s$ at the transition across the boundary curve:

$$\left(\frac{\partial p}{\partial v}\right)_s^{\sigma\,\text{two-ph}}-\left(\frac{\partial p}{\partial v}\right)_s^{\sigma\,\text{one-ph}}$$
$$=\left[\left(\frac{\partial T}{\partial v}\right)_s^{\sigma\,\text{two-ph}}-\left(\frac{\partial T}{\partial v}\right)_s^{\sigma\,\text{one-ph}}\right]\frac{ds_\sigma}{dv}. \tag{7.136}$$

Bearing in mind that

$$\left(\frac{\partial T}{\partial v}\right)_s=-\left(\frac{\partial T}{\partial s}\right)_v\left(\frac{\partial s}{\partial v}\right)_T, \tag{7.137}$$

$$\frac{ds_\sigma}{dv}=\frac{ds_\sigma}{dT}\frac{dT}{dv_\sigma}, \tag{7.138}$$

and taking into account (4.3), (5.101a) and (7.18), from (7.136) we obtain

$$\left(\frac{\partial p}{\partial v}\right)_s^{\sigma\,\text{two-ph}}-\left(\frac{\partial p}{\partial v}\right)_s^{\sigma\,\text{one-ph}}$$
$$=c_s\left[\frac{1}{c_v^{\sigma\,\text{one-ph}}}\left(\frac{\partial p}{\partial T}\right)_v^{\sigma\,\text{one-ph}}-\frac{1}{c_v^{\sigma\,\text{two-ph}}}\frac{dp}{dT}\right]\frac{dT}{dv_\sigma}. \tag{7.139}$$

Combining this with (5.181) and (5.191), we obtain relations, respectively, for the discontinuity in the adiabatic exponent

$$k^{\sigma\,\text{two-ph}}-k^{\sigma\,\text{one-ph}}$$
$$=-\frac{c_s v_\sigma}{p}\left[\frac{1}{c_v^{\sigma\,\text{one-ph}}}\left(\frac{\partial p}{\partial T}\right)_v^{\sigma\,\text{one-ph}}-\frac{1}{c_v^{\sigma\,\text{two-ph}}}\frac{dp}{dT}\right]\frac{dT}{dv_\sigma} \tag{7.140}$$

and for the discontinuity in the sound velocity

$$(a^{\sigma\,\text{two-ph}})^2-(a^{\sigma\,\text{one-ph}})^2$$
$$=-c_3v_\sigma^2\left[\frac{1}{c_v^{\sigma\,\text{one-ph}}}\left(\frac{\partial p}{\partial T}\right)_v^{\sigma\,\text{one-ph}}-\frac{1}{c_v^{\sigma\,\text{two-ph}}}\frac{dp}{dT}\right]\frac{dT}{dv_\sigma}. \qquad (7.141)$$

It may seem that these relations are more convenient than Eqs. (7.101), (7.102), and (7.104), (7.105), since they enable us to calculate directly the discontinuities in the adiabatic exponent $k^\sigma$ and in the square of the sound velocity $(a^\sigma)^2$ and not $1/k^\sigma$ and $1/(a^\sigma)^2$. However, comparing Eqs. (7.101), (7.102) and (7.104), (7.105) with (7.140) and (7.141), we see that the former are considerably simpler.

The relations obtained above determine the discontinuities in the derivatives taken at the intersection of an isentrope with the boundary curve in the $v,T$-, $p,T$- and $p,v$-diagrams.

Together with Eq. (7.75), (7.76) and (7.83) through (7.86) for determining the discontinuity in the heat capacity $c_v$ in the event of a transition across the boundary curve, equations for the discontinuity in the quantity inverse to $c_v$ are interesting for certain cases. From (6.36) we obtain

$$\frac{1}{c_v^{\sigma\,\text{one-ph}}}-\frac{1}{c_v^{\sigma\,\text{two-ph}}}=\frac{1}{T}\,\frac{\left[\left(\dfrac{\partial T}{\partial v}\right)_s^{\sigma\,\text{two-ph}}-\left(\dfrac{\partial T}{\partial v}\right)_s^{\sigma\,\text{one-ph}}\right]^2}{\left(\dfrac{\partial p}{\partial v}\right)_s^{\sigma\,\text{two-ph}}-\left(\dfrac{\partial p}{\partial v}\right)_s^{\sigma\,\text{one-ph}}}, \qquad (7.142)$$

and from (6.41) we have

$$\frac{1}{c_v^{\sigma\,\text{one-ph}}}-\frac{1}{c_v^{\sigma\,\text{two-ph}}}$$
$$=\frac{T}{c_s^2}\left[\left(\frac{\partial p}{\partial v}\right)_s^{\sigma\,\text{two-ph}}-\left(\frac{\partial p}{\partial v}\right)_s^{\sigma\,\text{one-ph}}\right]\left(\frac{dv_\sigma}{dT}\right)^2. \qquad (7.143)$$

With the help of Eq. (7.130) we can easily see that these relations are identical.

## 7.6 Heat Capacities on Boundary Curves

7.6.1. We have already noted that the heat capacity along a boundary curve, $c_s$, is determined via (7.18)

$$c_s=T\frac{ds_\sigma}{dT},$$

where $ds_\sigma/dT$ is the total derivative along the boundary curve.

From Eqs. (6.4) and (6.5) we see that $ds_\sigma/dT$ can be written in the form of the following equivalent expressions:

$$\frac{ds_\sigma}{dT}=\left(\frac{\partial s}{\partial T}\right)_p^{\sigma\,\text{one-ph}}+\left(\frac{\partial s}{\partial p}\right)_T^{\sigma\,\text{one-ph}}\frac{dp}{dT}, \tag{7.144}$$

$$\frac{ds_\sigma}{dT}=\left(\frac{\partial s}{\partial T}\right)_v^{\sigma\,\text{one-ph}}+\left(\frac{\partial s}{\partial v}\right)_T^{\sigma\,\text{one-ph}}\frac{dv_\sigma}{dT}, \tag{7.145}$$

and

$$\frac{ds_\sigma}{dT}=\left(\frac{\partial s}{\partial T}\right)_s^{\sigma\,\text{two-ph}}+\left(\frac{\partial s}{\partial v}\right)_T^{\sigma\,\text{two-ph}}\frac{dv_\sigma}{dT}. \tag{7.146}$$

Bearing in mind (5.78a), (5.79a), (4.3), (4.4), and (7.48), we can transform these relations to

$$\frac{ds_\sigma}{dT}=\frac{c_p^{\sigma\,\text{one-ph}}}{T}-\left(\frac{\partial v}{\partial T}\right)_p^{\sigma\,\text{one-ph}}\frac{dp}{dT}, \tag{7.147}$$

$$\frac{ds_\sigma}{dT}=\frac{c_v^{\sigma\,\text{one-ph}}}{T}+\left(\frac{\partial p}{\partial T}\right)_v^{\sigma\,\text{one-ph}}\frac{dv_\sigma}{dT}, \tag{7.148}$$

and

$$\frac{ds_\sigma}{dT}=\frac{c_v^{\sigma\,\text{two-ph}}}{T}+\frac{dp}{dT}\frac{dv_\sigma}{dT}. \tag{7.149}$$

Taking these relations into account, from (7.18) we obtain for the left boundary curve

$$c_s'=c_p^{\prime\,\text{one-ph}}-T\left(\frac{\partial v}{dT}\right)_p^{\prime\,\text{one-ph}}\frac{dp}{dT}, \tag{7.150}$$

$$c_s'=c_v^{\prime\,\text{one-ph}}+T\left(\frac{\partial p}{\partial T}\right)_v^{\prime\,\text{one-ph}}\frac{dv'}{dT}, \tag{7.151}$$

$$c_s'=c_v^{\prime\,\text{two-ph}}+T\frac{dp}{dT}\frac{dv'}{dT}. \tag{7.152}$$

Similarly, for the right boundary curve

$$c_s''=c_p^{\prime\prime\,\text{one-ph}}-T\left(\frac{\partial v}{\partial T}\right)_p^{\prime\prime\,\text{one-ph}}\frac{dp}{dT}, \tag{7.153}$$

$$c_s''=c_v^{\prime\prime\,\text{one-ph}}+T\left(\frac{\partial p}{\partial T}\right)_v^{\prime\prime\,\text{one-ph}}\frac{dv''}{dT}, \tag{7.154}$$

$$c_s''=c_v^{\prime\prime\,\text{two-ph}}+T\frac{dp}{dT}\frac{dv''}{dT}. \tag{7.155}$$

These equations relate the heat capacities $c_s$, $c_p$, and $c_v$ on boundary curves.

7.6.2. From Eq. (3.28a) written as

$$Tds = dh - vdp$$

and taking into account (7.18), we can see that

$$c_s = \frac{dh_\sigma}{dT} - v_\sigma \frac{dp}{dT}. \tag{7.156}$$

This relation is most convenient for practical calculations of the heat capacity $c_s$.

7.6.3. We note that if we equate the right-hand sides of Eqs. (7.151) and (7.152) and, respectively, the right-hand sides of (7.154) and (7.155), we obtain Eqs. (7.75) and (7.76) for the discontinuity in the heat capacity $c_v$ on boundary curves.

On the other hand, equating the right-hand sides of Eqs. (7.150) and (7.151) and, respectively, the right-hand sides of (7.153) and (7.154), we obtain the equations for the difference in the heat capacities $c_p$ and $c_v$ on boundary curves on the one-phase side:

$$c_p'^{\,\text{one-ph}} - c_v'^{\,\text{one-ph}} = T\left[\left(\frac{\partial v}{\partial T}\right)_p'^{\,\text{one-ph}} \frac{dp}{dT} + \left(\frac{\partial p}{\partial T}\right)_v'^{\,\text{one-ph}} \frac{dv'}{dT}\right] \tag{7.157}$$

and

$$c_p''^{\,\text{one-ph}} - c_v''^{\,\text{one-ph}} = T\left[\left(\frac{\partial v}{\partial T}\right)_p''^{\,\text{one-ph}} \frac{dp}{dT} + \left(\frac{\partial p}{\partial T}\right)_v''^{\,\text{one-ph}} \frac{dv''}{dT}\right]. \tag{7.158}$$

We can easily show that these relations can transform to the type (5.109), i.e.

$$c_p'^{\,\text{one-ph}} - c_v'^{\,\text{one-ph}} = T\left(\frac{\partial p}{\partial T}\right)_v'^{\,\text{one-ph}} \left(\frac{\partial v}{\partial T}\right)_p'^{\,\text{one-ph}} \tag{7.159}$$

and

$$c_p''^{\,\text{one-ph}} - c_v''^{\,\text{one-ph}} = T\left(\frac{\partial p}{\partial T}\right)_v''^{\,\text{one-ph}} \left(\frac{\partial v}{\partial T}\right)_p''^{\,\text{one-ph}}. \tag{7.160}$$

Next, from (7.150) and (7.152) and, respectively, from (7.153) and (7.155), we obtain

$$c_p'^{\,\text{one-ph}} - c_v'^{\,\text{two-ph}} = T\frac{dp}{dT}\left[\left(\frac{\partial v}{\partial T}\right)_p'^{\,\text{one-ph}} + \frac{\partial v'}{\partial T}\right] \tag{7.161}$$

and

$$c_p''^{\,\text{one-ph}} - c_v''^{\,\text{two-ph}} = T\frac{dp}{dT}\left[\left(\frac{\partial v}{\partial T}\right)_p''^{\,\text{one-ph}} + \frac{dv''}{dT}\right]. \tag{7.162}$$

It is interesting to note that Eq. (7.161) was once used effectively to prove the inaccuracy of experimental data on the heat capacity $c_v$ for water given in one article. This was done as follows. Since both $(\partial v/\partial T)_p'^{\,\text{one-ph}}$ and $dv'/dT$ are positive (for water this is true at $T > 3.98°$ C), it follows from (7.161) that

$$c_p'^{\,\text{one-ph}} - c_v'^{\,\text{two-ph}} > 0. \tag{7.163}$$

Since comparison of the experimental data on the heat capacity $c_v'^{\,\text{two-ph}}$, given in the article, with the precise data on the heat capacity $c_p'^{\text{one-ph}}$ of water revealed that the values of $c_v'^{\text{two-ph}}$ are greater than those of $c_p'^{\text{one-ph}}$, the inadequacy of the experimental data on $c_v$ was proved.

## 7.7 Thermodynamic Quantities in a Two-Phase Region

7.7.1. As we noted in Sec. 7.1, those thermodynamic quantities that are the first derivatives of a thermodynamic potential ($v$, $s$, $u$, $h$, and $f$) are additive in a two-phase region:

$$v^{\text{two-ph}} = v'(1-x) + v''x, \tag{7.12}$$

$$s^{\text{two-ph}} = s'(1-x) + s''x, \tag{7.13}$$

$$u^{\text{two-ph}} = u'(1-x) + u''x, \tag{7.14}$$

$$h^{\text{two-ph}} = h'(1-x) + h''x, \tag{7.15}$$

$$f^{\text{two-ph}} = f'(1-x) + f''x. \tag{7.16}$$

As for quantities that are the second derivatives of a thermodynamic potential ($c_v$, $(\partial v/\partial p)_s$, $k$ and $a$ and others), their values in a two-phase region expressed in terms of thermodynamic quantities on the left and right boundary curves and the degree of dryness, $x$, are determined by the relations which we discuss below.

7.7.2. We start with $(\partial v/\partial p)_s$. Differentiating (7.12) with respect to pressure with $s$ kept constant, we obtain

$$\left(\frac{\partial v}{\partial p}\right)_s^{\text{two-ph}} = \frac{dv'}{dp}(1-x) + \frac{dv''}{dp}x + (v''-v')\left(\frac{\partial x}{\partial p}\right)_s. \tag{7.164}$$

In connection with this derivative we note the following. We calculate the partial derivative with respect to $p$ with $s$ kept constant, but since $v'$ and $v''$ as well as other quantities on the transition curve are functions of only one variable, the derivatives of $v'$ and $v''$ with respect to $p$ can only be total, i.e. $dv'/dp$ and $dv''/dp$.

Next, since in accordance with (7.17)

$$x = \frac{s-s'}{s''-s'},$$

differentiating this with respect to pressure with $s$ kept constant and taking into account the note on differentiating $v'$ and $v''$, we obtain

$$\left(\frac{\partial x}{\partial p}\right)_s = -\frac{1}{s''-s'}\left[\frac{ds'}{dp}(1-x) + \frac{ds''}{dp}x\right]. \tag{7.165}$$

Then, in accordance with (6.4) and (6.5), we can write

$$\frac{dv'}{dp} = \left(\frac{\partial v}{\partial p}\right)_s'^{\text{two-ph}} + \left(\frac{\partial v}{\partial s}\right)_p'^{\text{two-ph}} \frac{ds'}{dp} \tag{7.166}$$

and

$$\frac{dv''}{dp}=\left(\frac{\partial v}{\partial p}\right)_s^{''\,\text{two-ph}}+\left(\frac{\partial v}{\partial s}\right)_s^{''\,\text{two-ph}}\frac{ds''}{dp}. \qquad (7.167)$$

Bearing in mind Eqs. (4.2) and (7.51), we transform (7.166) and (7.167) to

$$\frac{dv'}{dp}=\left(\frac{\partial v}{\partial p}\right)_s^{'\,\text{two-ph}}+\frac{dT}{dp}\frac{ds'}{dp} \qquad (7.168)$$

and

$$\frac{dv''}{dp}=\left(\frac{\partial v}{\partial p}\right)_s^{''\,\text{two-ph}}+\frac{dT}{dp}\frac{ds''}{dp}. \qquad (7.169)$$

Substituting into Eq. (7.164) these expressions and also (7.165) for $(\partial x/\partial p)_s$ and taking into account that according to (7.22)

$$\frac{v''-v'}{s''-s'}=\frac{dT}{dp}, \qquad (7.170)$$

we obtain

$$\left(\frac{\partial v}{\partial p}\right)_s^{\text{two-ph}}=\left(\frac{\partial v}{\partial p}\right)_s^{'\,\text{two-ph}}(1-x)+\left(\frac{\partial v}{\partial p}\right)_s^{''\,\text{two-ph}}x. \qquad (7.171)$$

We see that $(\partial v/\partial p)_s$ in a two-phase region is additive, which is not obvious *a priori.*

Similarly, differentiating (7.12) with respect to $T$ with $s$ kept constant, we can show that

$$\left(\frac{\partial v}{\partial T}\right)_s^{\text{two-ph}}=\left(\frac{\partial v}{\partial T}\right)_s^{'\,\text{two-ph}}(1-x)+\left(\frac{\partial v}{\partial T}\right)_s^{''\,\text{two-ph}}x. \qquad (7.172)$$

The relation determining $(\partial v/\partial p)_s$ in a two-phase region can be obtained in another form. Equation (5.165)

$$\left(\frac{\partial p}{\partial v}\right)_s=\left(\frac{\partial p}{\partial v}\right)_T-\frac{T}{c_v}\left(\frac{\partial p}{\partial T}\right)_v^2$$

combined with (7.7) and (7.48) is written for a two-phase region thus:

$$\left(\frac{\partial p}{\partial v}\right)_s^{\text{two-ph}}=-\frac{T}{c_v^{\text{two-ph}}}\left(\frac{\partial p}{\partial T}\right)^2, \qquad (7.173)$$

whence

$$\left(\frac{\partial v}{\partial p}\right)_s^{\text{two-ph}}=-\frac{c_v^{\text{two-ph}}}{T}\left(\frac{\partial T}{\partial p}\right)^2, \qquad (7.174)$$

where $c_v^{\text{two-ph}}$ is the isochoric heat capacity in the two-phase region. We note that these interesting relations are almost unknown; they are extremely useful for calculating thermodynamic properties in the two-phase region.

We see that Eqs. (7.171) and (7.174), despite their apparent distinction, are identical. We can easily show this if we transform (7.171) in the following way: since it is obvious that

$$\left(\frac{\partial v}{\partial p}\right)_s=\left(\frac{\partial v}{\partial T}\right)_s\left(\frac{\partial T}{\partial p}\right)_s, \tag{7.175}$$

and, hence,

$$\left(\frac{\partial v}{\partial T}\right)_s=-\left(\frac{\partial v}{\partial s}\right)_T\left(\frac{\partial s}{\partial T}\right)_v, \tag{7.176}$$

it follows that allowing for the Maxwell equation (4.3a) and Eqs. (5.101a), (7.48) and (7.51), we can transform relation (7.175) for the two-phase region to (7.174).

From (7.171), in particular, it follows that

$$\left[\frac{\partial}{\partial v}\left(\frac{\partial v}{\partial p}\right)_s\right]_T=\frac{\left(\frac{\partial v}{\partial p}\right)_s''^{\text{ two-ph}}-\left(\frac{\partial v}{\partial p}\right)_s'^{\text{ two-ph}}}{v''-v'} \tag{7.177}$$

and from (7.174) that

$$\left[\frac{\partial}{\partial v}\left(\frac{\partial v}{\partial p}\right)_s\right]_T=-\frac{c_v''^{\text{ two-ph}}-c_v'^{\text{ two-ph}}}{T\,(v''-v')}\left(\frac{\partial p}{\partial T}\right)^2. \tag{7.178}$$

These (identical) relations determine the variation in $(\partial v/\partial p)_s$ along an isotherm in a two-phase region; we see that the dependence is linear (since the quantities on the right-hand sides of these equations remain constant on an isotherm).

7.7.3. We turn to the heat capacity $c_x$ of a two-phase mixture. The heat capacity of a two-phase mixture along the line of constant dryness, $x=\text{const}$, is determined in accordance with the general relation (5.99):

$$c_x=T\left(\frac{\partial s}{\partial T}\right)_x. \tag{7.179}$$

The equation for calculating $c_x$ from the known values of the thermodynamic quantities on the left and right boundary curves and the degree of dryness is obtained by differentiating relation (7.13) with respect to temperature with $x$ kept constant:

$$\left(\frac{\partial s}{\partial T}\right)_x=\frac{ds'}{dT}(1-x)+\frac{ds''}{dT}x. \tag{7.180}$$

Combining this with (7.18), we find that

$$c_x=c_s'(1-x)+c_s''x. \tag{7.181}$$

We see that

$$\left(\frac{\partial c_x}{\partial v}\right)_T=\frac{c_s''-c_s'}{v''-v'}. \tag{7.182}$$

7.7.4. Next we study $c_v$ in a two-phase region. Differentiating (7.14) with respect to $T$ with $v$ kept constant and taking into account the remark made in Sec. 7.7.2, we obtain

$$\left(\frac{\partial u}{\partial T}\right)_v^{\text{two-ph}}=\frac{du'}{dT}(1-x)+\frac{du''}{dT}x+(u''-u')\left(\frac{\partial x}{\partial T}\right)_v. \quad (7.183)$$

From (7.17)

$$x=\frac{v-v'}{v''-v'}$$

it follows that

$$\left(\frac{\partial x}{\partial T}\right)_v=-\frac{1}{v''-v'}\left[\frac{dv'}{dT}(1-x)+\frac{dv''}{dT}x\right]. \quad (7.184)$$

Taking into account that

$$\frac{du'}{dT}=\left(\frac{\partial u}{\partial T}\right)_v^{\prime\,\text{two-ph}}+\left(\frac{\partial u}{\partial v}\right)_T^{\prime\,\text{two-ph}}\frac{dv'}{dT}, \quad (7.185)$$

$$\frac{du''}{dT}=\left(\frac{\partial u}{\partial T}\right)_v^{\prime\prime\,\text{two-ph}}+\left(\frac{\partial u}{\partial v}\right)_T^{\prime\prime\,\text{two-ph}}\frac{dv''}{dT}; \quad (7.186)$$

$$\left(\frac{\partial u}{\partial T}\right)_v=c_v, \quad (5.107)$$

$$\left(\frac{\partial u}{\partial v}\right)_T=T\left(\frac{\partial p}{\partial T}\right)_v-p, \quad (5.2)$$

and, hence,

$$\left(\frac{\partial u}{\partial v}\right)_T^{\text{two-ph}}=T\frac{dp}{\partial T}-p, \quad (7.187)$$

from (7.183) we find that

$$c_v^{\text{two-ph}}=c_v^{\prime\,\text{two-ph}}(1-x)+c_v^{\prime\prime\,\text{two-ph}}x. \quad (7.188)$$

We see, for one, that

$$\left(\frac{\partial c_v^{\text{two-ph}}}{\partial v}\right)_T=\frac{c_v^{\prime\prime\,\text{two-ph}}-c_v^{\prime\,\text{two-ph}}}{v''-v'}. \quad (7.189)$$

Finally, if in (7.188) we substitute $c_v^{\prime\text{two-ph}}$ and $c_v^{\prime\prime\text{two-ph}}$ via (7.152) and (7.155), respectively:

$$c_v^{\prime\,\text{two-ph}}=c_s'-T\frac{dp}{dT}\frac{dv'}{dT} \quad (7.190)$$

and

$$c_v^{\prime\prime\,\text{two-ph}}=c_s''-T\frac{dp}{dT}\frac{dv''}{dT}, \quad (7.191)$$

we obtain an equation relating $c_v^{\prime\text{two-ph}}$ and $c_x$:

$$c_v^{\text{two-ph}}=c_x-T\frac{dp}{dT}\left[\frac{dv'}{dT}(1-x)+\frac{dv''}{dT}x\right]. \quad (7.192)$$

This equation implies that because an isochore does not coincide with a line $x = \text{const}$, i.e. due to the variation of the degree of dryness along an isochore (redistribution of substance between phases), the heat capacities $c_v^{\text{two-ph}}$ and $c_x$ differ from each other by the term on the right-hand side of Eq. (7.192).

7.7.5. Let us study the isentropic exponent in a two-phase region. In accordance with the general definition of the isentropic exponent (5.181)

$$k = -\frac{v}{p}\left(\frac{\partial p}{\partial v}\right)_s,$$

and taking into account (7.12) and (7.171), we obtain

$$k^{\text{two-ph}} = -\frac{v'(1-x)+v''x}{p\left[\left(\frac{\partial v}{\partial p}\right)_s^{\prime\,\text{two-ph}}(1-x)+\left(\frac{\partial v}{\partial p}\right)_s^{\prime\prime\,\text{two-ph}}x\right]}. \qquad (7.193)$$

Using Eqs. (7.174) and (7.188), we can write the relation determining the isentropic exponent inside the two-phase region in the following form:

$$k^{\text{two-ph}} = -\frac{T}{p}\,\frac{v'(1-x)+v''x}{c_v^{\prime\,\text{two-ph}}(1-x)+c_v^{\prime\prime\,\text{two-ph}}x}\left(\frac{dp}{dT}\right)^2. \qquad (7.194)$$

Other forms of this equation are also known. But the two equations (7.193) and (7.194) are the simplest in form, clear in their physical meaning, and useful for practical calculations.

7.7.6. We turn to the sound velocity in a two-phase region. The Laplace equation (5.191) for a two-phase region is

$$a^{\text{two-ph}} = \sqrt{-(v^{\text{two-ph}})^2\left(\frac{\partial p}{\partial v}\right)_s^{\text{two-ph}}}. \qquad (7.195)$$

Taking (7.12) and (7.171) into account, we can transform this equation to

$$a^{\text{two-ph}} = \frac{v'(1-x)+v''x}{\sqrt{-\left[\left(\frac{\partial v}{\partial p}\right)_s^{\prime\,\text{two-ph}}(1-x)+\left(\frac{\partial v}{\partial p}\right)_s^{\prime\prime\,\text{two-ph}}x\right]}}, \qquad (7.196)$$

while taking (7.174) into account, we can transform it to

$$a^{\text{two-ph}} = T\frac{dp}{dT}\,\frac{v'(1-x)+v''x}{\sqrt{T\left[c_v^{\prime\,\text{two-ph}}(1-x)+c_v^{\prime\prime\,\text{two-ph}}x\right]}}. \qquad (7.197)$$

These equations determine the sound velocity in the two-phase region from the known values of the thermodynamic quantities on the left and right boundary curves.[4]

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[4] Here we are speaking of the so-called *thermodynamic sound velocity*, i.e. the sound velocity at zero frequency. The question of the frequency dependence of the sound velocity in a two-phase region is beyond the scope of this book.

7.7.7. Finally, we discuss the behavior of the Joule-Thomson coefficient in a two-phase region. As noted in Sec. 7.4, in a two-phase region the Joule-Thomson coefficient has the same value along an isotherm for any value of $x$; namely, in accordance with (7.109),

$$\mu^{\text{two-ph}} = dT/dp.$$

We note in passing that the usual relation (5.139) for the Joule-Thomson coefficient

$$\mu = \frac{T\left(\frac{\partial v}{\partial T}\right)_p - v}{c_p}$$

makes no sense for a two-phase region, since in this case on the right-hand side of this relation, as follows from (7.8) and (7.90), there appears an indeterminate form of the $\infty/\infty$ type that cannot be evaluated.

## 7.8. Equations Relating Thermodynamic Quantities on the Left and Right Boundary Curves

7.8.1. The following equations relate thermodynamic quantities on the left and right boundary curves. We start with quantities that are first derivatives of a thermodynamic potential ($v$, $s$, $u$, $h$, and $f$).

The Clausius-Clapeyron equation (7.26) implies that

$$v'' - v' = \frac{r}{T}\frac{dT}{dp} \tag{7.198}$$

We recall that in accordance with (7.25)

$$s'' - s' = r/T \tag{7.199}$$

and in accordance with (7.24)

$$h'' - h' = r. \tag{7.200}$$

Since in accordance with (1.14a)

$$h = u + pv,$$

it follows that

$$u'' - u' = r - p\,(v'' - v'). \tag{7.201}$$

Combining this with (7.198), we obtain

$$u'' - u' = r\left(1 - \frac{p}{T}\frac{dT}{dp}\right). \tag{7.202}$$

Finally, since in accordance with (3.41)

$$f = u - Ts,$$

combining this with (7.201) and (7.25) we can write

$$f'' - f' = -p(v'' - v'). \tag{7.203}$$

We recall (see Sec. 7.1) that in a two-phase region $v$, $s$, $u$, $h$, and $f$ are additive, i.e. they change linearly with the degree of dryness $x$. Here, as we see from the above relations, the values of $v$, $s$, $u$ and $h$ are greater on the right boundary curve than on the left. As for $f$, from (7.203) we see that

$$f'' < f'. \tag{7.204}$$

This is not surprising, since from (3.41) if follows that

$$\left(\frac{\partial f}{\partial v}\right)_T = \left(\frac{\partial u}{\partial v}\right)_T - T\left(\frac{\partial s}{\partial v}\right)_T. \tag{7.205}$$

And since (5.2)

$$\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v - p$$

and (4.3)

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v,$$

are valid, it follows that

$$\left(\frac{\partial f}{\partial v}\right)_T = -p, \tag{7.206}$$

i.e. the free energy on an isotherm always decreases with increasing $v$.

This dependence has a clear physical meaning, too. We know that a system in an isothermal process performs work at the expense of its free energy. The phase transition requires work to be done and, hence, the free energy decreases as the degree of order in the system decreases.

7.8.2. From Eqs. (7.198) through (7.201) and (7.203) we can easily obtain equations relating the total derivatives of $v$, $s$, $u$, $h$ and $f$ with respect to temperature along boundary curves.

Differentiating (7.198), we obtain

$$\frac{dv''}{dT} - \frac{dv'}{dT} = (v'' - v')\left(\frac{1}{r}\frac{dr}{dT} - \frac{1}{T} - \frac{dT}{dp}\frac{d^2p}{dT^2}\right) \tag{7.207}$$

From (7.199) it follows that

$$\frac{ds''}{dT} - \frac{ds'}{dT} = \frac{1}{T}\left(\frac{dr}{dT} - \frac{r}{T}\right), \tag{7.208}$$

from (7.200) that

$$\frac{dh''}{dT} - \frac{dh'}{dT} = \frac{dr}{dT}, \tag{7.209}$$

from (7.201) that

$$\frac{du''}{dT}-\frac{du'}{dT}=\frac{dr}{dT}-\frac{r}{T}+p\,(v''-v')\left(\frac{1}{T}+\frac{dT}{dp}\,\frac{d^2p}{dT^2}-\frac{1}{r}\,\frac{dr}{dT}\right), \quad (7.210)$$

and from (7.203) that

$$\frac{df''}{dT}-\frac{df'}{dT}=(f''-f')\left(\frac{1}{r}\,\frac{dr}{dT}-\frac{1}{T}-\frac{dT}{dp}\,\frac{d^2p}{dT^2}\right)-\frac{r}{T}. \quad (7.211)$$

7.8.3. We turn to the equation relating the values of the heat capacity $c_s$ on boundary curves. As noted above, for the left and right boundary curves we have, respectively,

$$c_s'=T\,\frac{ds'}{dT} \quad (7.212)$$

and

$$c_s''=T\,\frac{ds''}{dT}. \quad (7.213)$$

Hence, it follows that

$$c_s''-c_s'=T\left(\frac{ds''}{dT}-\frac{ds'}{dT}\right). \quad (7.214)$$

Combining this with (7.208), we obtain

$$c_s''-c_s'=\frac{dr}{dT}-\frac{r}{T}. \quad (7.215)$$

This equation, sometimes called the *Clausius equation*, relates the values of $c_s$ on the left and right boundary curves.

Since the heat of vaporization decreases as the temperature increases, and, hence, $dr/dT<0$, it follows that always

$$c_s''-c_s'<0. \quad (7.216)$$

We recall that $c_s''$ for most substances is always negative.

Taking into account (7.215) and (7.198), we transform (7.182) to

$$\left(\frac{\partial c_x}{\partial v}\right)_T=\frac{dp}{dT}\left(\frac{T}{r}\,\frac{dr}{dT}-1\right). \quad (7.217)$$

Hence, it follows that $c_x$ on an isotherm decreases with increasing $v$.

7.8.4. Now let us discuss the equation relating the values of the heat capacity $c_p$ on boundary curves. As noted above, when the heat capacity $c_p$ crosses a boundary curve, it changes discontinuously from $c_p^{\sigma\,\text{two-ph}}$ at the point of intersection of an isobar with the boundary curve on the one-phase side to infinity in the two-phase region. Let us find the relation connecting $c_p''^{\,\text{one-ph}}$ and $c_p'^{\,\text{one-ph}}$.

In accordance with (7.205),

$$\frac{dh''}{dT}-\frac{dh'}{dT}=\frac{dr}{dT}.$$

We can write the expression for the total derivative of enthalpy on the saturation line with respect to temperature in accordance with (6.4) thus:

$$\frac{dh_\sigma}{dT}=\left(\frac{\partial h}{\partial T}\right)_p^{\sigma\ \text{one-ph}}+\left(\frac{\partial h}{\partial p}\right)_T^{\sigma\ \text{one-oh}}\frac{dp}{dT}. \tag{7.218}$$

Combining this with (5.106) and (5.11), we obtain

$$\frac{dh_\sigma}{dT}=c_p^{\sigma\ \text{one-ph}}+\left[v_\sigma-T\left(\frac{\partial v}{\partial T}\right)_p^{\sigma\ \text{one-ph}}\right]\frac{dp}{dT}. \tag{7.219}$$

Therefore, we can write

$$\frac{dh''}{dT}=c_p^{''\text{one-ph}}+\left[v''-T\left(\frac{\partial v}{\partial T}\right)_p^{''\text{one-ph}}\right]\frac{dp}{dT} \tag{7.220}$$

and

$$\frac{dh'}{dT}=c_p^{'\text{one-ph}}+\left[v'-T\left(\frac{\partial v}{\partial T}\right)_p^{'\text{one-ph}}\right]\frac{dp}{dT}. \tag{7.221}$$

Substituting $dh''/dT$ and $dh'/dT$ into (7.209), we obtain

$$c_p^{''\text{one-ph}}-c_p^{'\text{one-ph}}=\frac{dr}{dT}-(v''-v')\frac{dp}{dT}+T\left[\left(\frac{\partial v}{\partial T}\right)_p^{''\text{one-ph}}-\left(\frac{\partial v}{\partial T}\right)_p^{'\text{one-ph}}\right]\frac{dp}{dT}, \tag{7.222}$$

whence

$$c_p^{''\text{one-ph}}-c_p^{'\text{one-ph}}=\frac{dr}{dT}-\frac{r}{T}+T\left[\left(\frac{\partial v}{\partial T}\right)_p^{''\text{one-ph}}-\left(\frac{\partial v}{\partial T}\right)_p^{'\text{one-ph}}\right]\frac{dp}{dT}. \tag{7.223}$$

This equation relating $c_p^{''\text{one-ph}}$ and $c_p^{'\text{one-ph}}$ is sometimes called the *Planck equation*. It enables us to match the various values of $c_p^{\sigma\ \text{one-ph}}$ obtained as a result of independent measurements, and also to calculate the values of $c_p^{\sigma\ \text{one-ph}}$ on the other boundary curve from the known (for example, measured in an experiment) value of $c_p^{\sigma\ \text{one-ph}}$ on another boundary curve. For these purposes the Planck equation has been successfully used for water and water vapor.

We note that the Planck equation can also be obtained by substituting $c_s'$ and $c_s''$ from Eqs. (7.150) and (7.153) into (7.215).

We also note that Eq. (7.129) written as

$$c_p^{\sigma\ \text{one-ph}}=\frac{dh_\sigma}{dT}-\left[v_\sigma-T\left(\frac{\partial v}{\partial T}\right)_p^{\sigma\ \text{one-ph}}\right]\frac{dp}{dT} \tag{7.224}$$

is convenient for practical calculations of heat capacities on boundary curves.

The differential equations discussed in this chapter were derived for simple thermodynamic systems (i.e. systems performing only work of expansion) but can be generalized to various complex systems. In the next chapter we will discuss an equation similar to the Planck equation that relates the heat capacities of a superconductor in the superconducting and normal states at the phase transition point in the superconductor.

7.8.5. We derive an equation relating the values of the heat capacity $c_v$ on the boundary curve. As already noted, the isochoric heat capacity changes from the value of $c_v^{\sigma\ \text{one-ph}}$ on the one-phase side of the boundary curve to the value of $c_v^{\sigma\ \text{two-ph}}$ on the two-phase side. We can obtain the equation relating the values of $c_v^{\sigma\ \text{two-ph}}$ on the left and right boundary curves, $c_v''^{\text{two-ph}}$ and $c_v'^{\text{two-ph}}$, in the following way.

Differentiating (7.201) with respect to temperature, we obtain

$$\frac{du''}{dT}-\frac{du'}{dT}=T\left(v''-v'\right)\frac{d^2p}{dT^2}+\left(T\frac{dp}{dT}-p\right)\left(\frac{dv''}{dT}-\frac{dv'}{dT}\right). \tag{7.225}$$

In accordance with (6.4) the expression for total derivatives of internal energy on boundary curves with respect to temperature can be written, taking into account (7.48) thus:

$$\frac{du''}{dT}=c_v''^{\text{two-ph}}+\left(T\frac{dp}{dT}-p\right)\frac{dv''}{dT} \tag{7.226}$$

and

$$\frac{du'}{dT}=c_v'^{\text{two-ph}}+\left(T\frac{dp}{dT}-p\right)\frac{dv'}{dT}. \tag{7.227}$$

Substituting these values into (7.221), we obtain

$$c_v''^{\text{two-ph}}-c_v'^{\text{two-ph}}=T\left(v''-v'\right)\frac{d^2p}{dT^2}. \tag{7.228}$$

This relation can be obtained in another way. The well-known thermodynamic equation (5.128)

$$\left(\frac{\partial c_v}{\partial v}\right)_T=T\left(\frac{\partial^2p}{\partial T^2}\right)_v$$

combined with (7.48) for the two-phase region is written thus:

$$\left(\frac{\partial c_v^{\text{two-ph}}}{\partial v}\right)_T=T\frac{d^2p}{dT^2}. \tag{7.229}$$

Equating the right-hand sides of this equation and Eq. (7.189), we obtain (7.228).

From (7.228) we can see that for all substances always

$$c_v''^{\text{two-ph}}>c_v'^{\text{two-ph}}. \tag{7.230}$$

Let us now find an equation relating the values of $c_v$ on the right and left boundary curves on the one-phase side, $c_v'^{\text{one-ph}}$ and $c_v''^{\text{one-ph}}$. We can easily obtain the relation from (7.228), (7.84), and (7.86).

From (7.84) and (7.86) it follows that

$$c_v'^{\text{one-ph}} = c_v'^{\text{two-ph}} + T\left(\frac{\partial p}{\partial v}\right)_T'^{\text{one-ph}} \left(\frac{dv'}{dT}\right)^2 \tag{7.231}$$

and

$$c_v''^{\text{one-ph}} = c_v''^{\text{two-ph}} + T\left(\frac{\partial p}{\partial v}\right)_T''^{\text{one-ph}} \left(\frac{dv''}{dT}\right)^2. \tag{7.232}$$

Hence we see that

$$c_v''^{\text{one-ph}} - c_v'^{\text{one-ph}} = T\left[(v''-v')\frac{d^2p}{dT^2} + \left(\frac{\partial p}{\partial v}\right)_T''^{\text{one-ph}} \left(\frac{dv''}{dT}\right)^2 - \left(\frac{\partial p}{\partial v}\right)_T'^{\text{one-ph}} \left(\frac{dv'}{dT}\right)^2\right]. \tag{7.233}$$

The behavior of $c_v$ with $v$ on an isotherm on the boundaries and in a two-phase region is shown in Fig. 7.5, where *I* is the liquid region, *II* the two-phase region, and *III* the vapor region.

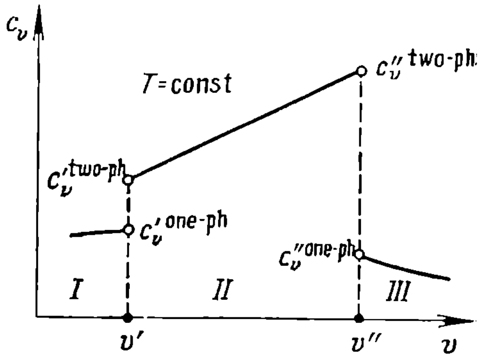

Fig. 7.5

Obviously, all equations relating the values of second derivatives of a thermodynamic potential on the left and right boundary curves on the one-phase side are similar in structure, i.e. in general they can be written thus:

$$y''^{\text{one-ph}} - y'^{\text{one-ph}} = \Delta y'' + (y''^{\text{two-ph}} - y'^{\text{two-ph}}) + \Delta y', \tag{7.234}$$

here $y$ is a thermodynamic function that is the second derivative of a potential, and $\Delta y$ the jump of this function in the transition across the boundary curve from the one-phase region to the two-phase region.

7.8.6. Let us discuss an equation relating the values of $(\partial v/\partial p)_s$ on boundary curves. Differentiating Eq. (7.198)

$$v'' - v' = \frac{r}{T}\frac{dT}{dp}$$

with respect to pressure, we obtain

$$\frac{dv''}{dp} - \frac{dv'}{dp} = \frac{1}{T}\frac{dr}{dp}\frac{dT}{dp} + \frac{r}{T}\frac{d^2T}{dp^2} - \frac{r}{T^2}\left(\frac{dT}{dp}\right)^2. \tag{7.235}$$

Substituting into this relation $dv'/dp$ from (7.168) and $dv''/dp$ from (7.169) and bearing in mind that the difference

$$\frac{ds''}{dp} - \frac{ds'}{dp}$$

combined with (7.199)

$$s'' - s' = r/T$$

can be written as

$$\frac{ds''}{dp} - \frac{ds'}{dp} = \frac{1}{T}\frac{dr}{dp} - \frac{r}{T^2}\frac{dT}{dp}, \tag{7.236}$$

from (7.235) we obtain

$$\left(\frac{\partial v}{\partial p}\right)_s^{\prime\prime\text{two-ph}} - \left(\frac{\partial v}{\partial p}\right)_s^{\prime\text{two-ph}} = \frac{r}{T}\frac{d^2T}{dp^2}. \tag{7.237}$$

This equation relates $(\partial v/\partial p)_s$ on the left and right boundary curves on the two-phase side. Since on the saturation line, as evidenced by the $p,T$-diagram,

$$\frac{d^2T}{dp^2} < 0 \tag{7.238}$$

and since, as we know, $(\partial v/\partial p)_s$ is always negative, it follows that always

$$\left|\left(\frac{\partial v}{\partial p}\right)_s^{\prime\prime\text{two-ph}}\right| > \left|\left(\frac{\partial v}{\partial p}\right)_s^{\prime\text{two-ph}}\right|. \tag{7.239}$$

The equation relating $(\partial v/\partial p)_s''^{\,\text{two-ph}}$ and $(\partial v/\partial p)_s'^{\,\text{two-ph}}$ can be written in another form. From (7.174) we see that

$$\left(\frac{\partial v}{\partial p}\right)_s^{\prime\text{two-ph}} = -\frac{c_v^{\prime\text{two-ph}}}{T}\left(\frac{dT}{dp}\right)^2 \tag{7.240}$$

and

$$\left(\frac{\partial v}{\partial p}\right)_s^{\prime\prime\text{two-ph}} = -\frac{c_v^{\prime\prime\text{two-ph}}}{T}\left(\frac{dT}{dp}\right)^2. \tag{7.241}$$

Hence, it follows that

$$\left(\frac{\partial v}{\partial p}\right)_s^{\prime\prime\text{two-ph}} - \left(\frac{\partial v}{\partial p}\right)_s^{\prime\text{two-ph}} = -\frac{c_v^{\prime\prime\text{two-ph}} - c_v^{\prime\text{two-ph}}}{T}\left(\frac{dT}{dp}\right)^2. \tag{7.242}$$

Combining this with (7.228), we obtain

$$\left(\frac{\partial v}{\partial p}\right)_s^{\prime\prime\text{two-ph}} - \left(\frac{\partial v}{\partial p}\right)_s^{\prime\text{two-ph}} = -(v'' - v')\left(\frac{dT}{dp}\right)^2\frac{d^2p}{dT^2}. \tag{7.243}$$

Equations (7.237) and (7.242) are, of course, equivalent. We can easily show this with the help of (7.11):

$$\frac{d^2p}{dT^2} = -\left(\frac{dp}{dT}\right)^3\frac{d^2T}{dp^2}.$$

We can now obtain an equation relating the values of $(\partial v/\partial p)_s$ on the left and right boundary curves on the one-phase side.

From (7.95) and (7.96) it follows that

$$\left(\frac{\partial v}{\partial p}\right)_s^{\prime\,\text{two-ph}} = \left(\frac{\partial v}{\partial p}\right)_s^{\prime\,\text{one-ph}} - \frac{c'_s}{Tc_p^{\prime\,\text{one-ph}}}\left(\frac{dT}{dp}\right)^2 \qquad (7.244)$$

and

$$\left(\frac{\partial v}{\partial p}\right)_s^{\prime\prime\,\text{two-ph}} = \left(\frac{\partial v}{\partial p}\right)_s^{\prime\prime\,\text{one-ph}} - \frac{c''_s}{Tc_p^{\prime\prime\,\text{one-ph}}}\left(\frac{dT}{dp}\right)^2 . \qquad (7.245)$$

Substituting $(\partial v/\partial p)_s^{\prime\,\text{two-ph}}$ and $(\partial v/\partial p)_s^{\prime\prime\,\text{two-ph}}$ into (7.237), we obtain

$$\left(\frac{\partial v}{\partial p}\right)_s^{\prime\prime\,\text{one-ph}} - \left(\frac{\partial v}{\partial p}\right)_s^{\prime\,\text{one-ph}}$$

$$= \frac{1}{T}\left[\left(\frac{c_s^{\prime\prime 2}}{c_p^{\prime\prime\,\text{one-ph}}} - \frac{c_s^{\prime 2}}{c_p^{\prime\,\text{one-ph}}}\right)\left(\frac{dT}{\partial p}\right)^2 + r\frac{d^2T}{dp^2}\right]. \qquad (7.246)$$

Taking into account (7.237), we can write the relation thus:

$$\left(\frac{\partial v}{\partial p}\right)_s^{\prime\prime\,\text{one-ph}} - \left(\frac{\partial v}{\partial p}\right)_s^{\prime\,\text{one-ph}}$$

$$= \frac{1}{T}\left(\frac{dT}{dp}\right)^2\left[\frac{c_s^{\prime\prime 2}}{c_p^{\prime\prime\,\text{one-ph}}} - \frac{c_s^{\prime 2}}{c_p^{\prime\,\text{one-ph}}} - (v'' - v')\frac{d^2p}{dT^2}\right]. \qquad (7.247)$$

These equations relate the values of $(\partial v/\partial p)_s$ on the left and right boundary curves on the one-phase side.

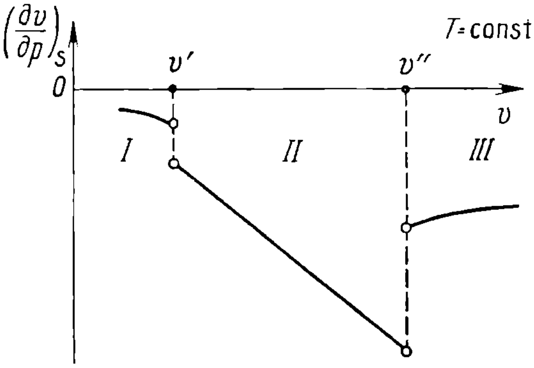

Fig. 7.6

The behavior of $(\partial v/\partial p)_s$ with $v$ on an isotherm on the boundaries and in a two-phase region is shown in Fig. 7.6 (the notations are the same as in Fig. 7.5).

7.8.7. We turn to an equation relating the values of isentropic exponent on the boundary curves. If we take into account (7.100)

$$\left(\frac{\partial v}{\partial p}\right)_s=-\frac{v}{kp},$$

from (7.237) we obtain

$$\frac{v''}{k''^{\text{two-ph}}}-\frac{v'}{k'^{\text{two-ph}}}=-\frac{rp}{T}\frac{d^2T}{dp^2}. \qquad (7.248)$$

Combining this with (7.242), we can write

$$\frac{v''}{k''^{\text{two-ph}}}-\frac{v'}{k'^{\text{two-ph}}}=p\,(v''-v')\left(\frac{dT}{dp}\right)^2\frac{d^2p}{dT^2}. \qquad (7.249)$$

These equations relate the values of the isentropic exponent on the left and right boundary curves on the two-phase side.

Next, from (7.245) we see that

$$\frac{v''}{k''^{\text{one-ph}}}-\frac{v'}{k'^{\text{one-ph}}}$$

$$=\frac{p}{T}\left[\left(\frac{c_s'^2}{c_p'^{\text{one-ph}}}-\frac{c_s''^2}{c_p''^{\text{one-ph}}}\right)\left(\frac{dT}{dp}\right)^2-r\frac{d^2T}{dp^2}\right]. \qquad (7.250)$$

Similarly, from (7.246) we obtain

$$\frac{v''}{k''^{\text{one-ph}}}-\frac{v'}{k'^{\text{one-ph}}}$$

$$=\frac{p}{T}\left(\frac{dT}{dp}\right)^2\left[\frac{c_s'^2}{c_p'^{\text{one-ph}}}-\frac{c_s''^2}{c_p''^{\text{one-ph}}}+(v''-v')\frac{d^2p}{dT^2}\right]. \qquad (7.251)$$

Such are the equations relating the values on the left and right boundary curves on the one-phase side.

7.8.8. We derive an equation relating the values of the sound velocity on boundary curves. Since in accordance with (7.103)

$$\left(\frac{\partial v}{\partial p}\right)_s=-\left(\frac{v}{a}\right)^2,$$

from (7.237) we find that

$$\left(\frac{v''}{a''^{\text{two-ph}}}\right)^2-\left(\frac{v'}{a'^{\text{two-ph}}}\right)^2=-\frac{r}{T}\frac{d^2T}{dp^2}. \qquad (7.252)$$

Similarly, from (7.243) it follows that

$$\left(\frac{v''}{a''^{\text{two-ph}}}\right)^2-\left(\frac{v'}{a'^{\text{two-ph}}}\right)^2=(v''-v')\left(\frac{dT}{dp}\right)^2\frac{d^2p}{dT^2}. \qquad (7.253)$$

These equations relate the values of the sound velocity on the left and right boundary curves on the two-phase side.

We can obtain an equation relating $a'^{\text{ two-ph}}$ and $a''^{\text{ two-ph}}$ explicitly, i.e. not as the difference in values of the inverse square of $a^{\sigma\text{ two-ph}}$ but the difference of squares of sound velocities on boundary curves. To this end we replace in the relation obvious from (7.103)

$$a^2 = -v^2 \left(\frac{\partial p}{\partial v}\right)_s \tag{7.254}$$

the values of the derivative using (7.173) and obtain

$$(a''^{\text{two-ph}})^2 - (a'^{\text{two-ph}})^2 = T\left(\frac{dp}{dT}\right)^2 \left(\frac{v''^2}{c_v''^{\text{two-ph}}} - \frac{v'^2}{c_v'^{\text{two-ph}}}\right). \tag{7.255}$$

This implies that always

$$a''^{\text{two-ph}} > a'^{\text{two-ph}}. \tag{7.256}$$

From (7.246) and (7.247) we obtain, respectively,

$$\left(\frac{v''}{a''^{\text{one-ph}}}\right)^2 - \left(\frac{v'}{a'^{\text{one-ph}}}\right)^2 = \frac{1}{T}\left[\left(\frac{c_s'^2}{c_p'^{\text{one-ph}}} - \frac{c_s''^2}{c_p''^{\text{one-ph}}}\right)\left(\frac{dT}{dp}\right)^2 - r\frac{d^2T}{dp^2}\right] \tag{7.257}$$

and

$$\left(\frac{v''}{a''^{\text{one-ph}}}\right)^2 - \left(\frac{v'}{a'^{\text{one-ph}}}\right)^2 = \frac{1}{T}\left[\frac{c_s'^2}{c_p'^{\text{one-ph}}} - \frac{c_s''^2}{c_p''^{\text{one-ph}}} + (v'' - v')\frac{d^2p}{dT^2}\right]. \tag{7.258}$$

These equations relate the values of the sound velocity on the left and right boundary curves on the one-phase side.

7.8.9. Finally, we derive an equation relating the values of the Joule-Thomson coefficient on boundary curves. We showed earlier (Eqs. (7.109) and (7.110)) that everywhere in the two-phase region the Joule-Thomson coefficient $\mu$ is the same and is

$$\mu^{\text{two-ph}} = \mu'^{\text{two-ph}} = \mu''^{\text{two-ph}} = \frac{dT}{dp}.$$

Taking this into account, from (7.111) and (7.112) we easily find that

$$\mu''^{\text{one-ph}} - \mu'^{\text{one-ph}} = \frac{1}{c_p'^{\text{one-ph}}}\frac{dh'}{dp} - \frac{1}{c_p''^{\text{one-ph}}}\frac{dh'}{dp}. \tag{7.259}$$

Using (2.8) and (7.109), we can write this relation in another form:

$$\frac{\mu''^{\text{one-ph}} - \mu'^{\text{one-ph}}}{\mu^{\text{two-ph}}} = \frac{1}{c_p'^{\text{one-ph}}}\frac{dh'}{dT} - \frac{1}{c_p''^{\text{one-ph}}}\frac{dh''}{dT}. \tag{7.260}$$

This equation relates the values of $\mu$ on the left and right boundary curves on the one-phase side.

7.8.10. We have found equations relating the values of basic thermodynamic quantities on the left and right boundary curves. The same approach can be used to obtain equations relating any other thermodynamic quantities.

The relations of this type are useful for the cases where the values of a thermodynamic quantity are obtained independently on the left and right boundary curves and we want to check how much these values are related thermodynamically. They are also useful when we know the values of a thermodynamic quantity on one of the boundary curves (usually on the liquid-phase side) and wish to calculate it on another boundary curve.

## 7.9 Equations for Second-Order Phase Transitions

7.9.1. In 1933 Paul Ehrenfest introduced the concept of a second-order phase transition.

An ordinary phase transition (according to Ehrenfest's classification, the first-order phase transition) is characterized, as we noted in Sec. 7.1, by a discontinuity in the first derivatives of $\varphi$:

$$v=\left(\frac{\partial\varphi}{\partial p}\right)_T \quad \text{and} \quad s=-\left(\frac{\partial\varphi}{\partial T}\right)_p .$$

The quantities $v$ and $s$ change discontinuously from the value in one of coexisting phases, $v^{(1)}$ and $s^{(1)}$, to the value in another phase, $v^{(2)}$ and $s^{(2)}$.

Ehrenfest called a transition in which the first derivatives of a thermodynamic potential are continuous a *second-order phase transition*, i.e.

$$v^{(1)} = v^{(2)} \tag{7.261}$$

and

$$s^{(1)} = s^{(2)}, \tag{7.262}$$

while the second derivatives of the potential change discontinuously, for instance,

$$\left(\frac{\partial s}{\partial T}\right)_p=-\left(\frac{\partial^2\varphi}{\partial T^2}\right)_p, \tag{7.263}$$

$$\left(\frac{\partial v}{\partial p}\right)_T=\left(\frac{\partial^2\varphi}{\partial p^2}\right)_T, \tag{7.264}$$

$$\left(\frac{\partial v}{\partial T}\right)_p=\left(\frac{\partial^2\varphi}{\partial T\,\partial p}\right). \tag{7.265}$$

The physical meaning of a second-order phase transition is beyond the scope of this book. Here we are interested only in the differential equations relating the second derivatives of a thermodynamic potential for coexisting phases in the event of a second-order phase transition. In other words, we wish to obtain equations determining the discontinuity of thermodynamic quantities on the line of a second-order phase transition.

In a second-order phase transition, just as in an ordinary phase transition, the two phases in the $p,T$-diagram are separated by a transition curve. In the $p,v$-, $T,v$-, $T,s$-, and $p,s$-diagrams we see that in a second-order phase transition the two phases are separated not by a two-phase region, as in an ordinary phase transition, but by a transition curve, since $v$ and $s$ at the point of a second-order transition change continuously.

We note that the transition from one phase to another across a second-order phase transition curve in the $p,v$-, $T,v$-, $T,s$-, and $p,s$-diagrams is similar to a first-order phase transition from a one-phase region to a two-phase region across a boundary curve (left or right). Indeed, in both cases the second derivatives of the potential change discontinuously. This implies that the relations describing the discontinuities in these quantities are similar in structure for both the boundary curves of an ordinary phase transition and the curves of a second-order phase transition.

7.9.2. The following second derivatives of the thermodynamic potential undergo a discontinuity on the second-order transition curve:

$$\left(\frac{\partial^2\varphi}{\partial T^2}\right)_p=-\left(\frac{\partial s}{\partial T}\right)_p=-\frac{c_p}{T}, \tag{7.266}$$

$$\left(\frac{\partial^2\varphi}{\partial p^2}\right)_T=\left(\frac{\partial v}{\partial p}\right)_T, \tag{7.267}$$

$$\frac{\partial^2\varphi}{\partial T\,\partial p}=\left(\frac{\partial v}{\partial T}\right)_p=-\left(\frac{\partial s}{\partial p}\right)_T, \tag{7.268}$$

$$\left[\frac{\partial}{\partial T}\left(\frac{\partial\varphi}{\partial T}\right)_p\right]_v=-\left(\frac{\partial s}{\partial T}\right)_v=-\frac{c_v}{T}, \tag{7.269}$$

$$\left[\frac{\partial}{\partial p}\left(\frac{\partial\varphi}{\partial p}\right)_T\right]_s=\left(\frac{\partial v}{\partial p}\right)_s, \tag{7.270}$$

$$\left[\frac{\partial}{\partial T}\left(\frac{\partial\varphi}{\partial p}\right)_T\right]_s=\left(\frac{\partial v}{\partial T}\right)_s=-\left(\frac{\partial s}{\partial p}\right)_v, \tag{7.271}$$

$$\left[\frac{\partial}{\partial v}\left(\frac{\partial\varphi}{\partial p}\right)_T\right]_T=-\left(\frac{\partial s}{\partial v}\right)_T=-\left(\frac{\partial p}{\partial T}\right)_v, \tag{7.272}$$

$$\left[\frac{\partial}{\partial v}\left(\frac{\partial\varphi}{\partial T}\right)_p\right]_p=-\left(\frac{\partial s}{\partial v}\right)_p=-\left(\frac{\partial p}{\partial T}\right)_s. \tag{7.273}$$

The same is true, naturally, for the inverse quantities.

In Chapter 6 we obtained the equations that give the discontinuities of these quantities, namely Eqs. (6.11), (6.13), (6.15), (6.16), (6.18), (6.20), (6.21), (6.23), (6.25), (6.26), (6.28), (6.30), (6.33) through (6.37), and (6.38) through (6.43) if the transition occurs in $p,v,T$ space or Eqs. (6.44) through (6.66) if it occurs in $\xi,w,T$ space. From these equations we can derive a group of relations that play the same role for second-order phase transitions as the Clausius-Clapeyron equation does for ordinary. These relations give the slope of the second-order transition curve in the $p,T$-, $p,v$-, $T,v$-, $p,s$-, $T,s$-, and $v,s$-diagrams.

From (6.31) and (6.32) it follows that[5]

$$\frac{dp}{dT}=\frac{c_p^{(2)}-c_p^{(1)}}{T\left[\left(\frac{\partial v}{\partial T}\right)_p^{(2)}-\left(\frac{\partial v}{\partial T}\right)_p^{(1)}\right]}=-\frac{\left(\frac{\partial v}{\partial T}\right)_p^{(2)}-\left(\frac{\partial v}{\partial T}\right)_p^{(1)}}{\left(\frac{\partial v}{\partial p}\right)_T^{(2)}-\left(\frac{\partial v}{\partial p}\right)_T^{(1)}}, \tag{7.274}$$

which is known as the *Ehrenfest equation*. Similarly, from (6.15) and (6.21) we find that

$$\frac{dT}{dv}=-\frac{\left(\frac{\partial p}{\partial T}\right)_s^{(2)}-\left(\frac{\partial p}{\partial T}\right)_s^{(1)}}{\left(\frac{\partial v}{\partial T}\right)_s^{(2)}-\left(\frac{\partial v}{\partial T}\right)_s^{(1)}}=-\frac{\left(\frac{\partial T}{\partial v}\right)_p^{(2)}-\left(\frac{\partial T}{\partial v}\right)_p^{(1)}}{\left(\frac{\partial T}{\partial p}\right)_v^{(2)}-\left(\frac{\partial T}{\partial p}\right)_v^{(1)}}, \tag{7.275}$$

from (6.13) and (6.26) that

$$\frac{dT}{dv}=-\frac{T\left[\left(\frac{\partial p}{\partial T}\right)_v^{(2)}-\left(\frac{\partial p}{\partial T}\right)_v^{(1)}\right]}{c_v^{(2)}-c_v^{(1)}}=-\frac{\left(\frac{\partial p}{\partial v}\right)_T^{(2)}-\left(\frac{\partial p}{\partial v}\right)_T^{(1)}}{\left(\frac{\partial p}{\partial T}\right)_v^{(2)}-\left(\frac{\partial p}{\partial T}\right)_v^{(1)}} \tag{7.276}$$

from (6.20) and (6.23) that

$$\frac{dp}{ds}=-\frac{\left(\frac{\partial T}{\partial p}\right)_s^{(2)}-\left(\frac{\partial T}{\partial p}\right)_s^{(1)}}{\left(\frac{\partial v}{\partial p}\right)_s^{(2)}-\left(\frac{\partial v}{\partial p}\right)_s^{(1)}}=-\frac{T\left[\left(\frac{1}{c_p}\right)^{(2)}-\left(\frac{1}{c_p}\right)^{(1)}\right]}{\left(\frac{\partial T}{\partial p}\right)_s^{(2)}-\left(\frac{\partial T}{\partial p}\right)_s^{(1)}}, \tag{7.277}$$

from (6.18) and (6.28) that

$$\frac{dT}{ds}=-\frac{\left(\frac{\partial T}{\partial p}\right)_v^{(2)}-\left(\frac{\partial T}{\partial p}\right)_v^{(1)}}{\left(\frac{\partial v}{\partial T}\right)_s^{(2)}\left(\frac{\partial v}{\partial T}\right)_s^{(1)}}=\frac{\left(\frac{\partial T}{\partial v}\right)_p^{(2)}-\left(\frac{\partial T}{\partial v}\right)_p^{(1)}}{\left(\frac{\partial p}{\partial T}\right)_s^{(2)}-\left(\frac{\partial p}{\partial T}\right)_s^{(1)}}, \tag{7.278}$$

and from (6.25) and (6.30) that

$$\frac{dv}{ds}=-\frac{T\left[\left(\frac{1}{c_v}\right)^{(2)}-\left(\frac{1}{c_v}\right)^{(1)}\right]}{\left(\frac{\partial T}{\partial v}\right)_s^{(2)}-\left(\frac{\partial T}{\partial v}\right)_s^{(1)}}=\frac{\left(\frac{\partial T}{\partial v}\right)_s^{(2)}-\left(\frac{\partial T}{\partial v}\right)_s^{(1)}}{\left(\frac{\partial p}{\partial v}\right)_s^{(2)}-\left(\frac{\partial p}{\partial v}\right)_s^{(1)}}. \tag{7.279}$$

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[5] The superscripts (1) and (2) denote the first and second coexisting phases, respectively, at the point of a second-order transition.

From Eqs. (6.38) through (6.41) we can obtain equations giving the slope of the second-order transition curve in the $p,T$-, $T,v$-, $p,s$-, and $v,s$-diagrams:

$$\frac{dp}{dT}=\sqrt{-\frac{c_p^{(2)}-c_p^{(1)}}{T\left[\left(\frac{\partial v}{\partial p}\right)_T^{(2)}-\left(\frac{\partial v}{\partial p}\right)_T^{(1)}\right]}}, \tag{7.280}$$

$$\frac{dT}{dv}=\sqrt{\frac{c_v^{(2)}-c_v^{(1)}}{T\left[\left(\frac{\partial p}{\partial v}\right)_T^{(2)}-\left(\frac{\partial p}{\partial v}\right)_T^{(1)}\right]}}, \tag{7.281}$$

$$\frac{dp}{ds}=\sqrt{\frac{T\left[\left(\frac{1}{c_p}\right)^{(2)}-\left(\frac{1}{c_p}\right)^{(1)}\right]}{\left(\frac{\partial v}{\partial p}\right)_s^{(2)}-\left(\frac{\partial v}{\partial p}\right)_s^{(1)}}}, \tag{7.282}$$

and

$$\frac{dv}{ds}=\sqrt{-\frac{T\left[\left(\frac{1}{c_v}\right)^{(2)}-\left(\frac{1}{c_v}\right)^{(1)}\right]}{\left(\frac{\partial p}{\partial v}\right)_s^{(2)}-\left(\frac{\partial p}{\partial v}\right)_s^{(1)}}}. \tag{7.283}$$

Similarly, for the second-order phase transition in the $\xi,w,T$ space we can obtain relations giving the slope of the transition curve in the $\xi,T$-, $\xi,w$-, $T,w$-, $\xi,s$-, $T,s$-, $w,s$-diagrams.

From (6.44) and (6.47) we find that

$$\frac{d\xi}{dT}=\frac{c_\xi^{(2)}-c_\xi^{(1)}}{\left[T\left(\frac{\partial w}{\partial T}\right)_\xi^{(2)}-\left(\frac{\partial w}{\partial T}\right)_\xi^{(1)}\right]}=-\frac{\left(\frac{\partial w}{\partial T}\right)_\xi^{(2)}-\left(\frac{\partial w}{\partial T}\right)_\xi^{(1)}}{\left(\frac{\partial w}{\partial \xi}\right)_T^{(2)}-\left(\frac{\partial w}{\partial \xi}\right)_T^{(1)}}, \tag{7.284}$$

from (6.46) and (6.50) that

$$\frac{d\xi}{dw}=\frac{\left(\frac{\partial \xi}{\partial T}\right)_s^{(2)}-\left(\frac{\partial \xi}{\partial T}\right)_s^{(1)}}{\left(\frac{\partial w}{\partial T}\right)_s^{(2)}-\left(\frac{\partial w}{\partial T}\right)_s^{(1)}}=-\frac{\left(\frac{\partial T}{\partial w}\right)_\xi^{(2)}-\left(\frac{\partial T}{\partial w}\right)_\xi^{(1)}}{\left(\frac{\partial T}{\partial \xi}\right)_w^{(2)}-\left(\frac{\partial T}{\partial \xi}\right)_w^{(1)}} \tag{7.285}$$

from (6.45) and (6.53) that

$$\frac{dT}{dw}=-\frac{T\left[\left(\frac{\partial \xi}{\partial T}\right)_w^{(2)}-\left(\frac{\partial \xi}{\partial T}\right)_w^{(1)}\right]}{c_w^{(2)}-c_w^{(1)}}=-\frac{\left(\frac{\partial \xi}{\partial w}\right)_T^{(2)}-\left(\frac{\partial \xi}{\partial w}\right)_T^{(1)}}{\left(\frac{\partial \xi}{\partial T}\right)_w^{(2)}-\left(\frac{\partial \xi}{\partial T}\right)_w^{(1)}}, \tag{7.286}$$

from (6.49) and (6.51) that

$$\frac{d\xi}{ds}=-\frac{\left(\frac{\partial T}{\partial \xi}\right)_s^{(2)}-\left(\frac{\partial T}{\partial \xi}\right)_s^{(1)}}{\left(\frac{\partial w}{\partial \xi}\right)_s^{(2)}-\left(\frac{\partial w}{\partial \xi}\right)_s^{(1)}}=-\frac{T\left[\left(\frac{1}{c_\xi}\right)^{(2)}-\left(\frac{1}{c_\xi}\right)^{(1)}\right]}{\left(\frac{\partial T}{\partial \xi}\right)_s^{(2)}-\left(\frac{\partial T}{\partial \xi}\right)_s^{(1)}}, \tag{7.287}$$

from (6.48) and (6.54) that

$$\frac{dT}{ds}=-\frac{\left(\frac{\partial T}{\partial \xi}\right)_w^{(2)}-\left(\frac{\partial T}{\partial \xi}\right)_w^{(1)}}{\left(\frac{\partial w}{\partial T}\right)_s^{(2)}-\left(\frac{\partial w}{\partial T}\right)_s^{(1)}}=\frac{\left(\frac{\partial T}{\partial w}\right)_\xi^{(2)}-\left(\frac{\partial T}{\partial w}\right)_\xi^{(1)}}{\left(\frac{\partial \xi}{\partial T}\right)_s^{(2)}-\left(\frac{\partial \xi}{\partial T}\right)_s^{(1)}}, \tag{7.288}$$

and from (6.52) and (6.55) that

$$\frac{dw}{ds}=-\frac{T\left[\left(\frac{1}{c_w}\right)^{(2)}-\left(\frac{1}{c_w}\right)^{(1)}\right]}{\left(\frac{\partial T}{\partial w}\right)_s^{(2)}-\left(\frac{\partial T}{\partial w}\right)_s^{(1)}}=\frac{\left(\frac{\partial T}{\partial w}\right)_s^{(2)}-\left(\frac{\partial T}{\partial w}\right)_s^{(1)}}{\left(\frac{\partial \xi}{\partial w}\right)_s^{(2)}-\left(\frac{\partial \xi}{\partial w}\right)_s^{(1)}}. \tag{7.289}$$

From (6.61) through (6.64) we obtain, respectively,

$$\frac{d\xi}{dT}=\sqrt{-\frac{c_\xi^{(2)}-c_\xi^{(1)}}{T\left[\left(\frac{\partial w}{\partial \xi}\right)_T^{(2)}-\left(\frac{\partial w}{\partial \xi}\right)_T^{(1)}\right]}}, \tag{7.290}$$

$$\frac{dw}{dT}=\sqrt{\frac{c_w^{(2)}-c_w^{(1)}}{T\left[\left(\frac{\partial \xi}{\partial w}\right)_T^{(2)}-\left(\frac{\partial \xi}{\partial w}\right)_T^{(1)}\right]}}, \tag{7.291}$$

$$\frac{d\xi}{ds}=\sqrt{\frac{T\left[\left(\frac{1}{c_\xi}\right)^{(2)}-\left(\frac{1}{c_\xi}\right)^{(1)}\right]}{\left(\frac{\partial w}{\partial \xi}\right)_s^{(2)}-\left(\frac{\partial w}{\partial \xi}\right)_s^{(1)}}}, \tag{7.292}$$

and

$$\frac{dw}{ds}=\sqrt{-\frac{T\left[\left(\frac{1}{c_w}\right)^{(2)}-\left(\frac{1}{c_w}\right)^{(1)}\right]}{\left(\frac{\partial \xi}{\partial w}\right)_s^{(2)}-\left(\frac{\partial \xi}{\partial w}\right)_s^{(1)}}}. \tag{7.293}$$

These are the basic relationships for second-order phase transitions.

7.9.3. Now we will show how these relations can be applied to a second-order phase transition in a superconductor without an external magnetic field.

From (7.31) it follows that the heat of the phase transition from the superconducting to the normal state is

$$q = -\frac{TH_{\text{cr}}v_{\text{super}}}{4\pi}\frac{dH_{\text{cr}}}{dT}. \tag{7.294}$$

This shows that when $H_{\text{cr}} = 0$ (i.e. at $T = T_{\text{cr}}$), the heat of the phase transition vanishes (experiments show that $dH_{\text{cr}}/dT$ is finite for any temperature). Thus, an ordinary phase transition in a superconductor without an external magnetic field becomes a second-order phase transition. On the curve representing the transition from the superconducting to the normal state the point where $H_{\text{cr}} = 0$ is singular.

Equations describing this second-order phase transition can be obtained from (6.44) through (6.66) if we assume that $\xi = -H$ and $w = j$. In particular, Eq. (6.61) for the discontinuity of the heat capacity with the generalized force kept constant can be written for this case as

$$c_H^{\text{super}} - c_H^{\text{norm}} = -T\left[\left(\frac{\partial j_{\text{super}}}{\partial H}\right)_T - \left(\frac{\partial j_{\text{norm}}}{\partial H}\right)_T\right]\left(\frac{dH_{\text{cr}}}{dT}\right)^2. \tag{7.295}$$

Bearing in mind that, in accordance with (7.30)

$$j_{\text{super}} = -v_{\text{super}}H/4\pi$$

and that, as we noted in Sec. 7.2,

$$j_{\text{norm}} = 0, \tag{7.296}$$

we obtain

$$\left(\frac{\partial j_{\text{super}}}{\partial H}\right)_T = -\frac{1}{4\pi}\left[\left(\frac{\partial v_{\text{super}}}{\partial H}\right)_T H + v_{\text{super}}\right] \tag{7.297}$$

and

$$\left(\frac{\partial j_{\text{norm}}}{\partial H}\right)_T = 0. \tag{7.298}$$

Experiments show that the specific volume of a superconductor in the superconducting state varies very little with the strength of an external magnetic field (there is no magnetostriction); in other words,

$$\left(\frac{\partial v_{\text{super}}}{\partial H}\right)_T = 0. \tag{7.299}$$

Taking into account (7.297) through (7.299), from (7.295) we obtain

$$c_H^{\text{super}} - c_H^{\text{norm}} = \frac{v_{\text{super}} T}{4\pi} \left( \frac{dH_{\text{cr}}}{dT} \right)^2 . \tag{7.300}$$

This equation determines the magnitude of the discontinuity in the heat capacity $c_{\text{norm}}$ for the phase transition from the superconducting to the normal state in the absence of an external magnetic field. It is called the *Rutger equation* and shows that, since its right-hand side is always positive, the heat capacity $c_{\text{norm}}$ at the phase transition from the superconducting to the normal state drops suddenly.

# 8 The Mathematics of the Critical Point

## 8.1 Thermodynamic Relations for the Critical Point

8.1.1. The point on the saturation line where the liquid and vapor phases become indistinguishable is known as the critical point. It is the final point on the line of the liquid-vapor phase transition, which begins at the triple point. We will denote thermodynamic parameters at the critical point by $p_{\mathrm{cr}}$, $T_{\mathrm{cr}}$, $v_{\mathrm{cr}}$, etc.

In accordance with what we have just said,

$$v'' - v' = 0 \tag{8.1}$$

at the critical point and, hence,

$$v'' = v' = v_{\mathrm{cr}}. \tag{8.2}$$

The heat of vaporization, $r$, also vanishes at the critical point. This follows from the Clausius-Clapeyron equation (7.198). If we write (7.198) as

$$r = T\,(v'' - v')\frac{dp}{dT}, \tag{8.3}$$

combining this with (8.1) and bearing in mind that $dp/dT$ cannot be infinite, we see that at the critical point

$$r = 0. \tag{8.4}$$

From experiments we know that the critical isotherm ($T_{\mathrm{cr}}$ = const) has in the $p$, $v$-diagram a horizontal inflectional tangent at the critical point and, hence,

$$\left(\frac{\partial p}{\partial v}\right)_T^{\mathrm{cr}} = 0, \tag{8.5}$$

$$\left(\frac{\partial^2 p}{\partial v^2}\right)_T^{\mathrm{cr}} = 0. \tag{8.6}$$

Similarly, experimental data shows that the following lines have at the critical point a horizontal inflectional tangent: an isobar in the $T$,$v$-diagram, so that

$$\left(\frac{\partial T}{\partial v}\right)_p^{\mathrm{cr}} = 0 \tag{8.7}$$

and

$$\left(\frac{\partial^2 T}{\partial v^2}\right)_p^{\mathrm{cr}}=0; \tag{8.8}$$

an isotherm in the $p,s$-diagram, so that

$$\left(\frac{\partial p}{\partial s}\right)_T^{\mathrm{cr}}=0 \tag{8.9}$$

and

$$\left(\frac{\partial^2 p}{\partial s^2}\right)_T^{\mathrm{cr}}=0, \tag{8.10}$$

an isobar in the $T,s$-diagram, so that

$$\left(\frac{\partial T}{\partial s}\right)_p^{\mathrm{cr}}=0 \tag{8.11}$$

and

$$\left(\frac{\partial^2 T}{\partial s^2}\right)_p^{\mathrm{cr}}=0, \tag{8.12}$$

an isobar in the $T,h$-diagram, so that

$$\left(\frac{\partial T}{\partial h}\right)_p^{\mathrm{cr}}=0 \tag{8.13}$$

and

$$\left(\frac{\partial^2 T}{\partial h^2}\right)_p^{\mathrm{cr}}=0, \tag{8.14}$$

finally, an isotherm in the $p,h$-diagram, so that

$$\left(\frac{\partial p}{\partial h}\right)_T^{\mathrm{cr}}=0 \tag{8.15}$$

and

$$\left(\frac{\partial^2 p}{\partial h^2}\right)_T^{\mathrm{cr}}=0. \tag{8.16}$$

Combining (8.11) with (5.100) or, which is the same, (8.13) with (5.106), we find that

$$c_p^{\mathrm{cr}}=\infty. \tag{8.17}$$

We note that the derivative of pressure on the saturation line with respect to temperature at the critical point $(dp/dT)_{\mathrm{cr}}$ and the derivative of pressure with respect to temperature on the isochore $v=v_{\mathrm{cr}}$ at the critical point $(\partial p/\partial T)_v^{\mathrm{cr}}$ are finite; this is clear from the physical meaning of these quantities.

The behavior of the corresponding curves in the phase diagrams at the critical point is schematically shown in Fig. 8.1.

We note that Eqs. (8.7) through (8.17) do not represent different independent properties of a substance at the critical point. In the final analysis, all these relations describe one experimental fact: that the critical isotherm in the $p,v$-diagram has a horizontal inflectional tangent at the critical point; whence, we can obtain Eqs. (8.7) through (8.17) from (8.5) and (8.6).

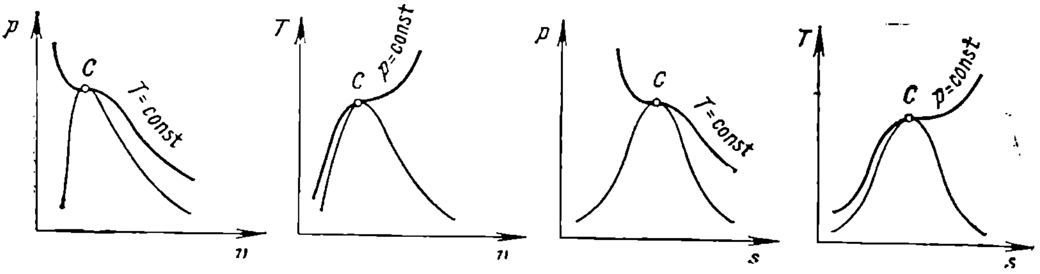

Fig. 8.1

Let us show this by an example. We will obtain (8.7) and (8.8) from (8.5) and (8.6). From (2.68) we see that

$$\left(\frac{\partial T}{\partial v}\right)_p = -\left(\frac{\partial T}{\partial p}\right)_v \left(\frac{\partial p}{\partial v}\right)_T. \tag{8.18}$$

Since, as noted earlier, $(\partial p/\partial T)_v^{\text{cr}}$ is finite, combining (8.18) with (8.5) yields (8.7).

Next, we determine the value of $(\partial^2 T/\partial v^2)_p$. Differentiating (8.18) with respect to $v$ with $p$ kept constant, we obtain

$$\left(\frac{\partial^2 T}{\partial v^2}\right)_p = -\frac{\partial^2 T}{\partial p\,\partial v}\left(\frac{\partial p}{\partial v}\right)_T - \left(\frac{\partial T}{\partial p}\right)_v \left[\frac{\partial}{\partial v}\left(\frac{\partial p}{\partial v}\right)_T\right]_p. \tag{8.19}$$

In accordance with (2.71) we write

$$\left[\frac{\partial}{\partial v}\left(\frac{\partial p}{\partial v}\right)_T\right]_p = \left[\frac{\partial}{\partial v}\left(\frac{\partial p}{\partial v}\right)_T\right]_T + \left[\frac{\partial}{\partial T}\left(\frac{\partial p}{\partial v}\right)_T\right]_v \left(\frac{\partial T}{\partial v}\right)_p, \tag{8.20}$$

or, which is the same,

$$\left[\frac{\partial}{\partial v}\left(\frac{\partial p}{\partial v}\right)_T\right]_p = \left(\frac{\partial^2 p}{\partial v^2}\right)_T + \frac{\partial^2 p}{\partial T\,\partial v}\left(\frac{\partial T}{\partial v}\right)_p. \tag{8.21}$$

Taking into account (8.21), from (8.19) we obtain

$$\left(\frac{\partial^2 T}{\partial v^2}\right)_p = -\frac{\partial^2 T}{\partial p\,\partial v}\left(\frac{\partial p}{\partial v}\right)_T + \left(\frac{\partial^2 p}{\partial v^2}\right)_T + \frac{\partial^2 p}{\partial T\,\partial v}\left(\frac{\partial T}{\partial v}\right)_p. \tag{8.22}$$

An analysis of the experimental $p,v,T$-data for the near-critical region shows unambiguously that $(\partial^2 T/\partial p\,\partial v)^{\text{cr}}$ and $(\partial^2 p/\partial T\,\partial v)^{\text{cr}}$

are not infinite.[1] Taking this into account and bearing in mind (8.5), (8.6), and (8.7), from (8.22) we obtain (8.8).

Similarly, if we combine the Maxwell equation (4.4a) with (8.7), we obtain relation (8.9) and so on.

8.1.2. Experimental data shows (see Fig. 8.1) that the total derivative of the specific volume on the saturation line with respect to temperature, $dv_\sigma/dT$, become infinite at the critical point. It is obvious that

$$\lim_{T_\sigma \to T_{\mathrm{cr}}} \frac{dv'}{dT} = \infty, \tag{8.23}$$

and

$$\lim_{T_\sigma \to T_{\mathrm{cr}}} \frac{dv''}{dT} = -\infty. \tag{8.24}$$

Since according to (2.8)

$$\frac{dv}{dp} = \frac{dv}{dT}\frac{dT}{dp}, \tag{8.25}$$

and, as already noted, $dT/dp$ is finite at the critical point, combining this equation with (8.23) and (8.24) yields relations for $dv'/dp$ and $dv''/dp$ similar to (8.23) and (8.24).

Similarly, $ds_\sigma/dT$ is infinite at the critical point, and here (see Fig. 8.1)

$$\lim_{T_\sigma \to T_{\mathrm{cr}}} \frac{ds'}{dT} = \infty, \tag{8.26}$$

$$\lim_{T_\sigma \to T_{\mathrm{cr}}} \frac{ds''}{dT} = -\infty. \tag{8.27}$$

Combining these with (7.18), we find that

$$\lim_{T_\sigma \to T_{\mathrm{cr}}} c'_s = \infty, \tag{8.28}$$

$$\lim_{T_\sigma \to T_{\mathrm{cr}}} c''_s = -\infty. \tag{8.29}$$

Since

$$\frac{ds}{dp} = \frac{ds}{dT}\frac{dT}{dp}, \tag{8.30}$$

taking into account the above remarks, we obtain relations for $ds'/dp$ and $ds''/dp$ similar to (8.26) and (8.27). The situation is the same with $dh_\sigma/dT$, $du_\sigma/dT$, and $df_\sigma/dT$ at the critical point.

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[1] Whether these quantities are zero or nonzero remains open to question, but it is clear that they cannot be infinite.

From the given relations it is clear (see Fig. 8.1) that

$$\left(\frac{dT}{dv_\sigma}\right)_{\text{cr}}=0, \qquad (8.31)$$

$$\left(\frac{dT}{ds_\sigma}\right)_{\text{cr}}=0, \qquad (8.32)$$

$$\left(\frac{dp}{dv_\sigma}\right)_{\text{cr}}=0, \qquad (8.33)$$

$$\left(\frac{dp}{ds_\sigma}\right)_{\text{cr}}=0. \qquad (8.34)$$

There is an interesting and important question concerning the curvature of the boundary curve at the critical point, i.e. the values of the second derivatives, such as $(d^2T/dv^2)_{\text{cr}}$ and $(d^2T/ds^2)_{\text{cr}}$. Experimental data (see Fig. 8.1) would seem to show, at first glance, that these derivatives are finite and negative at the critical point. However, it is argued that $(d^2T/dv^2)_{\text{cr}}$ and $(d^2T/ds^2)_{\text{cr}}$ and other similar derivatives are zero. This question cannot be solved unambiguously due to the reasons to be discussed in Sec. 8.2.

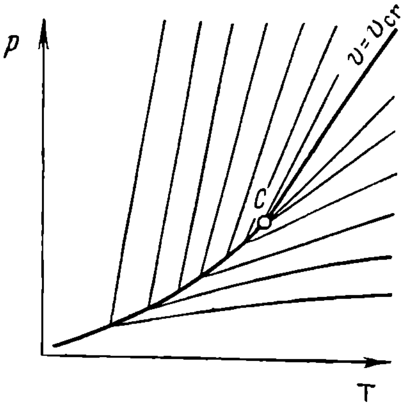

Fig. 8.2

8.1.3. Experimental data shows that at the critical point the saturation line in the $p,T$-diagram matches smoothly, without a salient point, the critical isochore ($v_{\text{cr}}$ = const) (Fig. 8.2). This means that

$$\left(\frac{dp}{dT}\right)_{\text{cr}}=\left(\frac{\partial p}{\partial T}\right)^{\sigma}_{v_{\text{cr}}}, \qquad (8.35)$$

which is known as the *Planck-Gibbs equation*, or *rule*.

Extensive experimental data for a great variety of substances prove the validity of Eq. (8.35). Let us derive this equation analytically.

In accordance with (2.81) we can write

$$\frac{dp}{dT}=\left(\frac{\partial p}{\partial T}\right)^{\sigma}_{v}+\left(\frac{\partial p}{\partial v}\right)^{\sigma}_{T}\frac{dv_\sigma}{dT}. \qquad (8.36)$$

From (8.5), (8.22), and (8.23) it follows that for the critical point there appears an indeterminate form $0\cdot\infty$ in the second term on the right-hand side of (8.36). We will try to evaluate the indeterminate form by L'Hospital's rule. To this end we write (8.36) as

$$\frac{dp}{dT}-\left(\frac{\partial p}{\partial T}\right)^{\sigma}_{v}=\frac{\left(\frac{\partial p}{\partial v}\right)^{\sigma}_{T}}{\frac{dT}{dv_\sigma}} \qquad (8.37)$$

and take the derivatives of the numerator and denominator on the right-hand side of this relation. The peculiar feature is that the numerator contains the partial derivative with respect to $v$ with $T$ kept constant, while the denominator contains the total derivative with respect to $v$ along the saturation line. But it is obvious that we must take the derivative of the same form of both the numerator and denominator. Therefore, we take the total derivative of the numerator and denominator with respect to $v$. Then (8.37) yields

$$\lim_{T\to T_{\mathrm{cr}}}\left[\frac{dp}{dT}-\left(\frac{\partial p}{\partial T}\right)_v^\sigma\right]=\lim_{T\to T_{\mathrm{cr}}}\frac{\dfrac{d}{dv_\sigma}\left(\dfrac{\partial p}{\partial v}\right)_T^\sigma}{\dfrac{d^2T}{dv_\sigma^2}}. \tag{8.38}$$

For the quantity in the numerator on the right-hand side of (8.38), it follows from (2.81) that

$$\frac{d}{dv_\sigma}\left(\frac{\partial p}{\partial v}\right)_T^\sigma=\left[\frac{\partial}{\partial v}\left(\frac{\partial p}{\partial v}\right)_T^\sigma\right]_T+\left[\frac{\partial}{\partial T}\left(\frac{\partial p}{\partial v}\right)_T^\sigma\right]_v\frac{dT}{dv_\sigma}, \tag{8.39}$$

or, which is the same,

$$\frac{d}{dv_\sigma}\left(\frac{\partial p}{\partial v}\right)_T^\sigma=\left(\frac{\partial^2 p}{\partial v^2}\right)_T^\sigma+\left(\frac{\partial^2 p}{\partial T\,\partial v}\right)^\sigma\frac{dT}{dv_\sigma}. \tag{8.40}$$

If we combine this with (8.38), we can write

$$\lim_{T\to T_{\mathrm{cr}}}\left[\frac{dp}{dT}-\left(\frac{\partial p}{\partial T}\right)_v^\sigma\right]=\lim_{T\to T_{\mathrm{cr}}}\frac{\left(\dfrac{\partial^2 p}{\partial v^2}\right)_T^\sigma+\left(\dfrac{\partial^2 p}{\partial T\,\partial v}\right)^\sigma\dfrac{dT}{dv_\sigma}}{\dfrac{d^2T}{dv_\sigma^2}}. \tag{8.41}$$

Taking into account (8.6) and (8.31) and bearing in mind that $(\partial^2 p/\partial T\ \partial v)^{\mathrm{cr}}$ is finite and $(d^2T/dv^2)_{\mathrm{cr}}$ is nonzero, from (8.41) we obtain the Planck-Gibbs equation (8.35).

We note that this derivation is valid so far as $(d^2T/dv^2)_{\mathrm{cr}}$ is nonzero. Otherwise on the right-hand side of (8.41) there appears an indeterminate form 0/0 that cannot be evaluated. However, the brilliant experimental verification of the validity of the Planck-Gibbs equation (8.35) can be considered an argument for the statement that $(d^2T/dv^2)_{\mathrm{cr}}$ is nonzero. Nevertheless, the given derivation of the Planck-Gibbs equation cannot be regarded as rigorous because the value of $(d^2T/dv^2)_{\mathrm{cr}}$ remains undefined.

8.1.4. The Planck-Gibbs equation can be generalized to caloric state surfaces. By the method similar to the one given above we can show that

$$\left(\frac{dp}{dT}\right)_{\mathrm{cr}}=\left(\frac{\partial p}{\partial T}\right)_s^{\mathrm{cr}}=\left(\frac{\partial p}{\partial T}\right)_u^{\mathrm{cr}}=\left(\frac{\partial p}{\partial T}\right)_h^{\mathrm{cr}}=\left(\frac{\partial p}{\partial T}\right)_f^{\mathrm{cr}}. \tag{8.42}$$

This relation implies that at the critical point the lines $s$ = const, $u$ = const, $h$ = const, and $f$ = const, just as the critical isochore, have a common tangent with the saturation line.

These relations are completely verified by experimental data (Fig. 8.3). To derive these relations we must bear in mind the notes on the curvature of the boundary curve at the critical point that were made for the derivation of Eq. (8.35).

8.1.5. The experimental data on the $p,v,T$-dependence shows that the critical isochore near the critical point is almost a straight line.

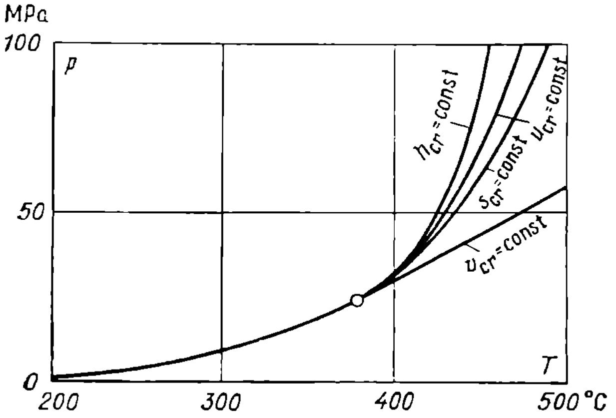

Fig. 8.3

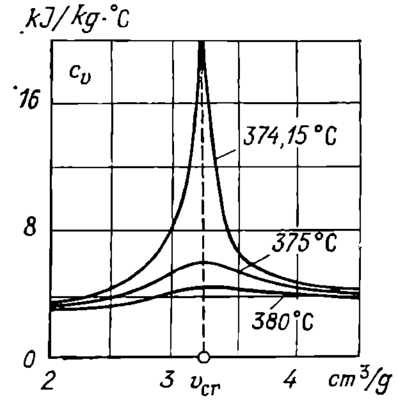

Fig. 8.4

This is verified by the experimental data on the heat capacity $c_v$: the values of $c_v$ on the critical and near-critical isotherms on the $c_v$, $v$-diagram pass through the maximum at $v = v_{cr}$ (this is illustrated by the experimental data for water in Fig. 8.4); consequently, in the near-critical region

$$\left(\frac{\partial c_v}{\partial v}\right)_T = 0, \tag{8.43}$$

and since according to (5.128)

$$\left(\frac{\partial c_v}{\partial v}\right)_T = T\left(\frac{\partial^2 p}{\partial T^2}\right)_v, \tag{8.44}$$

it follows that near the critical point

$$\left(\frac{\partial^2 p}{\partial T^2}\right)_{v_{cr}} = 0. \tag{8.45}$$

(With the increase in temperature the critical isochore becomes increasingly steeper.)

8.1.6. We also note that Eq. (5.165)

$$\left(\frac{\partial p}{\partial v}\right)_s = \left(\frac{\partial p}{\partial v}\right)_T - \frac{T}{c_v}\left(\frac{\partial p}{\partial T}\right)_v^2$$

combined with (8.5) and (8.35) for the critical point assumes the following form:

$$\left(\frac{\partial p}{\partial r}\right)_s^{\mathrm{cr}} = -\frac{T_{\mathrm{cr}}}{c_v^{\mathrm{cr}}}\left(\frac{dp}{dT}\right)_{\mathrm{cr}}^2. \tag{8.46}$$

8.1.7. The thermodynamic behavior of pure substances at the critical point has so far been studied insufficiently. Essentially, we know very little about the critical point. Above we noted what facts can be regarded as firmly established: at the critical point the first and second derivatives of pressure with respect to volume or entropy at $T$ constant and of temperature with respect to volume or entropy at $p$ constant vanish, the heat capacity $c_p$ is infinite, and the saturation line and critical isochore match smoothly (the Planck-Gibbs rule). This scant list probably exhausts all the reliable facts which we have relating to a thermodynamic analysis of the critical point of a pure substance.

Much more extensive is the list of questions that have not yet been answered:

(a) Do the derivatives $(\partial^3 p/\partial v^3)_T^{\mathrm{cr}}$, $(\partial^4 p/\partial v^4)_T^{\mathrm{cr}}$, etc. have zero or nonzero values?

(b) Does the mixed derivative $(\partial^2 p/\partial T\ \partial v)^{\mathrm{cr}}$ have a zero or nonzero value?

(c) Do such quantities as the heat capacity $c_v$ and the sound velocity $a$ undergo a continuous or discontinuous change when passing through the critical point?

(d) What is the behavior of the curvature of the boundary curve at the critical point, i.e. are the second derivatives $(d^2T/dv^2)_{\mathrm{cr}}$, $(d^2T/ds^2)_{\mathrm{cr}}$, etc. nonzero, and what is the saturation line curvature at the critical point in the $p,T$-diagram, i.e. is the value of $(d^2p/dT^2)_{\mathrm{cr}}$ zero or nonzero?

(e) Is the heat capacity $c_v$ finite or infinite at the critical point? And correspondingly (see Eq. (8.46) with due regard for (5.191)) is the sound velocity equal to zero at the critical point?

In spite of the categorical statements of some authors, a detailed analysis shows that there are no unambiguous answers to these and a number of other related questions.

The reader probably noticed that in this section we often use such phrases as "experimental data shows that" while the differential equations of thermodynamics are almost not used. We must understand that practically all relations given in this section are no more than a simple statement of the results of experiments. The few relations derived in this section are either not flawless from the point of view of the strictness of their derivation (the Planck-Gibbs equation is not flawless because we do not know exactly whether $(d^2T/dv^2)_{\mathrm{cr}}$ differs from zero, and Eq. (8.45) because we do not know whether

$c_v^{\mathrm{cr}}$ is finite) or useless for an analysis of the critical point (Eq. (8.46) because we are uncertain about the value of $c_v^{\mathrm{cr}}$). The means that we have at our disposal for analyzing the critical point are scanty, while for an analysis of the behavior of a substance on the boundaries and in a two-phase region there is a wide variety of thermodynamic relations.

What is the reason for this peculiarity of the problem of describing thermodynamic properties of a substance at the critical point among other problems of thermodynamics? Let us examine these questions in detail.

## 8.2 Describing the Thermodynamic Properties of a Substance at the Critical Point

8.2.1. The complexity of the problem of a thermodynamic description of the critical point given in Sec. 8.1.7 is explained by the singular behavior of the critical point on the thermodynamic state surface of a substance. If we use differential equations for the critical point, which are valid for all the other states of a substance, there appear in many relations (as a result of this singularity) indeterminate forms that cannot be evaluated. Due to these forms the mathematical tools of thermodynamics begin to "slip" at the critical point. This difficulty is basic: it is not that unambiguous proof of the statements of the thermodynamics of the critical point under discussion has not been found as yet, as a nonspecialist may think, but that in principle ordinary differential equations do not enable us to find such proof or relations for the critical point by a rigorous method.

Here is an example to show that it is useless to try to solve the problems of thermodynamics of the critical point with the help of ordinary differential equations of thermodynamics. We will try to establish whether the discontinuity in the heat capacity $c_v$ retains its value or vanishes at the critical point when crossing the boundary curve.

Recall that the value of the discontinuity in $c_v$ on the boundary curve is determined by Eqs. (7.84) and (7.86), which we can write thus:

$$c_v^{\sigma\ \text{two-ph}} - c_v^{\sigma\ \text{one-ph}} = T\left(\frac{\partial p}{\partial v}\right)_T^{\sigma}\left(\frac{dv_\sigma}{dT}\right)^2. \tag{8.47}$$

If we combine this with (8.5), (8.23), and (8.24) in order to determine the quantity $\Delta c_v = c_v^{\sigma\ \text{two-ph}} - c_v^{\sigma\ \text{one-ph}}$ at the critical point, we see that on the right-hand side of Eq. (8.47) there appears an indeterminate form $0 \cdot \infty$. Let us evaluate this indeterminate form by L'Hospital's rule. If we write Eq. (8.47) as

$$\frac{c_v^{\sigma\,\text{one-ph}} - c_v^{\sigma\,\text{two-ph}}}{T} = \frac{\left(\frac{\partial p}{\partial v}\right)_T^{\sigma}}{\left(\frac{\partial T}{dv_\sigma}\right)^2}, \tag{8.48}$$

we can differentiate the numerator and denominator on the right-hand side of this relation by taking the total derivatives with respect to $v$:

$$\lim_{T \to T_{\text{cr}}} \frac{c_v^{\sigma\,\text{one-ph}} - c_v^{\sigma\,\text{two-ph}}}{T} = \lim_{T \to T_{\text{cr}}} \frac{\frac{d}{dv_\sigma}\left(\frac{\partial p}{\partial v}\right)_T^{\sigma}}{2\frac{dT}{dv_\sigma}\frac{d^2T}{dv_\sigma^2}}. \tag{8.49}$$

Using (8.40), we can transform this relation to

$$\lim_{T \to T_{\text{cr}}} \frac{c_v^{\sigma\,\text{one-ph}} - c_v^{\sigma\,\text{two-ph}}}{T} = \lim_{T \to T_{\text{cr}}} \frac{\left(\frac{\partial^2 p}{\partial v^2}\right)_T^{\sigma} + \left(\frac{\partial^2 p}{\partial T\,\partial v}\right)^{\sigma}\frac{dT}{dv_\sigma}}{2\frac{dT}{dv_\sigma}\frac{d^2T}{\partial v_\sigma^2}}. \tag{8.50}$$

Taking into account (8.6) and (8.31) and the above-mentioned remarks about the quantities $(\partial^2 p/\partial T\,\partial v)^{\text{cr}}$ and $(d^2T/dv^2)_{\text{cr}}$, we see that on the right-hand side of Eq. (8.50) there again appears an indeterminate form 0/0. Further attempts to evaluate this indeterminate form do not yield a positive result.

Thus, the mathematical tools of thermodynamics do not enable us to evaluate indeterminate forms in the ordinary thermodynamic relations if we apply them to the critical point. Meanwhile, even today some authors state in all sincerity that using the ordinary differential equations of thermodynamics they have managed to formulate certain new conclusions about the thermodynamic properties of a substance at the critical point. Understandably, a thorough analysis always reveals some mistake in such works. In this connection we must realize that if any work claims to have obtained new conclusions about the properties of substances at the critical point using ordinary differential equations of thermodynamics, it must contain a more or less veiled mathematical mistake.

8.2.2. We must call attention especially to a typical mathematical error often encountered in works on the thermodynamics of the critical point. The reason for this error is a stereotype that researchers acquire while studying mathematical analysis. As we know from analysis, the second derivative of a function at the point of inflection is zero. But this statement has one exception important for the thermodynamic treatment of the critical point.

We wrote relation (8.6) and others similar to it for the critical point on the basis of the above-mentioned statement of mathematical analysis. It may seem that we can write $(\partial^2 v/\partial p^2)_T^{\mathrm{cr}} = 0$ for the critical point with the same degree of reliability as we did for (8.6), since here we also speak of the second derivative at the point of inflection of the function. The situation with $(\partial^2 v/\partial p^2)_T^{\mathrm{cr}}$, however, is far more complex than it may seem at first glance. Let us examine the $(\partial v/\partial p)_T$ versus $p$ and the $v$ versus $p$ dependence on the critical isotherm (Fig. 8.5). The graphs in Fig. 8.5 show that since the quantity $(\partial v/\partial p)_T$ becomes infinite when approaching the critical point both from the left and from the right, in other words, undergoes a discontinuity of the first kind at the critical point, the derivative $(\partial(\partial v/\partial p)_T/\partial p)_T = (\partial^2 v/\partial p^2)_T$ is not defined at the critical point. Therefore, the relation $(\partial^2 v/\partial p^2)_T^{\mathrm{cr}} = 0$ is absolutely unjustified. It is obvious that the situation is the same with all the functions that have a vertical tangent at the point of inflection, i.e. an infinite first derivative. And since, as already noted (see Fig. 8.1), the critical isotherms in the $v,p$-; $s,p$-, and $h,p$-diagrams and the critical isobars in the $v$, $T$-, $s$, $T$-; and $h,T$-diagrams are just such functions, we must always bear in mind this characteristic feature when applying thermodynamic relations to the critical point.

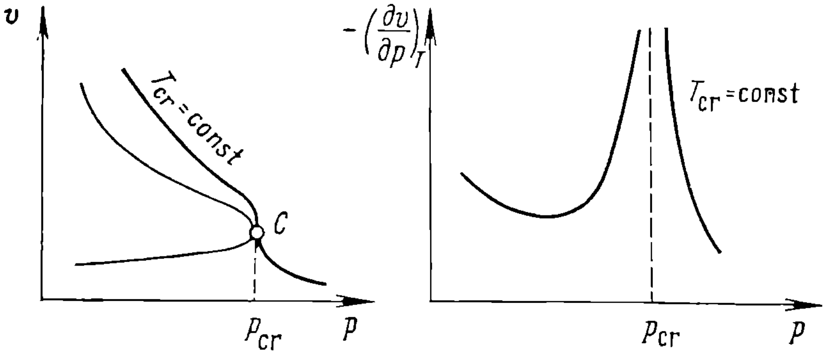

Fig. 8.5

8.2.3. The following question is in order. If the differential equations of thermodynamics do not make it possible to arrive at unambiguous conclusions concerning the properties of a substance at the critical point, then why cannot we analyze these properties by a precision experiment?

Unfortunately, the accuracy of experimental data rapidly diminishes when approaching the critical point. This is explained not by an imperfection of measuring devices but by difficulties of a fundamental nature. The point is that for an overwhelming majority of thermodynamic quantities the so-called reference error of the measured quantity becomes infinite with the approach to the critical point. Therefore, we cannot overcome mathematical complexities solely by a direct experiment.

8.2.4. We cannot discuss here the interesting attempts to describe the properties of a substance at the critical point by the methods of statistical physics as well as by the methods of scaling theory because, first, this is beyond the scope of this book and, second, the degree of reliability of the results obtained by these methods is not well-defined.

8.2.5. But how can we advance in describing the thermodynamic properties of a substance at its critical point? Progress in solving this problem can be achieved only by developing special mathematical tools suitable for examining this singular point on the thermodynamic state surface of a substance.

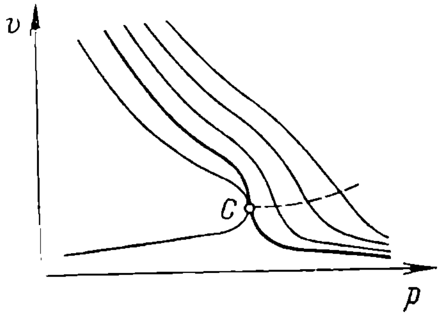

Fig. 8.6

8.2.6. In conclusion, one more interesting observation may be made concerning the problem of investigating the critical point even though it may seem controversial. If at present we have no mathematical tools for operating with such singularities as the critical point, it may prove effective to use formally nonrigorous limiting relations (each time, of course, substantiating the possibility of their application). By limiting relations we mean the application to the critical point of relations that are strictly valid however near this point.

Here is an example to explain this. As we have noted before, the quantity $(\partial^2 v/\partial p^2)_T$ cannot be defined at the critical point by ordinary methods. However, everywhere along the line of inflection points of the isotherms (we know from the experiment that as this line approaches the critical point, it smoothly matches with the critical isotherm; Fig. 8.6) the equality

$$\left(\frac{\partial^2 v}{\partial p^2}\right)_T = 0 \tag{8.51}$$

is satisfied up to the critical point. Thus, (8.51) is valid arbitrarily near the critical point. Right at the critical point the critical isotherm has an inflection, too. These circumstances, possibly, enable us to apply (8.51) to the critical point proper.

Next, it is easy to notice the characteristic feature that the isobar-isotherms in a two-phase region acquire all the peculiarities typical of the critical point. Indeed, since in the $p,v$-, $T,v$-, $p,s$-, $T,s$-, $p,h$-, and $T,h$-diagrams an isobar-isotherm in the two-phase region is a horizontal line, the relations similar to (8.5) through (8.18) are valid for it. The relations (7.68) are similar to Planck-Gibbs equations (8.36) and (8.43). This enables us to assume that the critical point, which is a limiting point in the two-phase region, acquires all the peculiarities typical of isobar-isotherms in the two-phase region. This is not surprising, since the critical point is, in essence, a degenerated (subtended to zero) isobaric-isothermal straight line. If this statement is valid, then, for one, for the critical point we can use the relation obvious for the two-phase region

$$\left(\frac{\partial^2 p}{\partial T \cdot \partial v}\right)^{\text{two-ph}} = 0 \qquad (8.52)$$

and similar relations.

Such methods of examining the thermodynamic properties of the critical point are less preferable, of course, than the one mentioned in Sec. 8.2.5, due to the insufficiently rigorous nature of the statements used. However, until special mathematical tools suitable for examining the critical point have been found, such a method may be considered justified and useful. The history of physics knows many cases when tools nonrigorous from the mathematical point of view did not prevent obtaining conclusions whose substantiation was given subsequently.

Such an approach can be justified by the analogy with the well-known method of determining a function at the point of discontinuity of the first kind. We recall that a discontinuity of the first kind is where the function is, strictly speaking, not defined but limits to this function exist on both sides of the point of discontinuity; these limits are taken as the values of the function at the point of discontinuity.

In conclusion we stress once more that the observations made in Sec. 8.2.6 should not be regarded as indisputable. Nevertheless, their detailed discussion, which is beyond the scope of this book, could be useful.

Any further investigations of difficult but interesting problems of thermodynamics of the critical point are, obviously, of great importance.

# 9 Complex Thermodynamic Systems

## 9.1 The Basic Thermodynamic Relations for Complex Systems

9.1.1. In Sec. 1.1 we agreed to call thermodynamic systems performing other work besides work of expansion complex systems. In this chapter we will consider only complex systems performing no more than two types of work simultaneously, one being the work of expansion. For such systems the differential of work performed by the system is given by (1.8)

$$dL = pdV + \xi dW,$$

or in (mass) specific values by (1.8a)

$$dl = pdv + \xi dw,$$

where $\xi$ is the generalized force with the exception of pressure, and $W$ (the mass specific value is $w$) is the generalized coordinate with the exception of volume.

The combined equation of the first and second laws of thermodynamics for the complex systems under consideration is written in the form (1.30)

$$TdS = dU + pdV + \xi dW,$$

or in (mass) specific values in the form (1.30a)

$$Tds = du + pdv + \xi dw.$$

The Maxwell equations for complex systems were obtained in Sec. 4.2. For mass specific quantities these are (4.17), (4.18), (4.20), (4.21), (4.23), (4.24), (4.26), and (4.27); similar equations are derived for the entire system.

9.1.2. We will obtain differential equations describing the behavior of different specific complex systems by a single method, namely, by using Eqs. (1.30), or (1.30a), the Maxwell equations and the equation of state of the given complex system.

Detailed analysis of the thermodynamic peculiarities of complex systems exceeds the limits of this book.[1] Therefore, below we give only the basic relations for different complex systems.

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[1] For detailed analysis of these problems see the book: V.V. Sychev, *Complex Thermodynamic Systems*, Mir Publishers, Moscow, 1981.

## 9.2 Systems in a Magnetic Field

9.2.1. We know that for a magnetic substance in a magnetic field the magnetic field strength taken with a minus sign, $-H$, is the generalized force, $\xi$, and the magnetization of the substance, $j$, is the generalized coordinate, $w$.

Hence, the combined equation of the first and second laws of thermodynamics (Eq. (1.30a)) for a system in a magnetic field is written as follows:

$$T\,ds = du + p\,dv - H\,dj. \tag{9.1}$$

Combining this with the Legendre transformation (3.48), we see that

$$T\,ds = dh^* - v\,dp + j\,dH, \tag{9.2}$$

where

$$h^* = u + pv - Hj, \tag{9.3}$$

which is the enthalpy of a system in a magnetic field (see Eq. (1.15a)).

In accordance with (4.17a), (4.20), (4.23a), and (4.26) we can write the Maxwell equations for a system in a magnetic field as

$$\left(\frac{\partial j}{\partial T}\right)_{s,\,v} = \left(\frac{\partial s}{\partial H}\right)_{j,\,v}, \tag{9.4}$$

$$\left(\frac{\partial j}{\partial s}\right)_{H,\,p} = -\left(\frac{\partial T}{\partial H}\right)_{s,\,p}, \tag{9.5}$$

$$\left(\frac{\partial j}{\partial s}\right)_{T,\,v} = -\left(\frac{\partial T}{\partial H}\right)_{j,\,v}, \tag{9.6}$$

$$\left(\frac{\partial j}{\partial T}\right)_{H,\,p} = \left(\frac{\partial s}{\partial H}\right)_{T,\,p}. \tag{9.7}$$

We know from physics that the equation of state of a magnetic substance that relates magnetization to magnetic field strength is written thus

$$j = \chi H, \tag{9.8}$$

where $\chi$ is the mass specific magnetic susceptibility.

9.2.2. If we combine (9.1) with (9.6) and (9.8), we find that

$$\left(\frac{\partial u}{\partial j}\right)_{T,v} = \frac{j}{\chi}\left[1 + \frac{T}{\chi}\left(\frac{\partial \chi}{\partial T}\right)_{j,\,v}\right]. \tag{9.9}$$

Similarly, combining (9.2) with (9.7) and (9.8), we obtain

$$\left(\frac{\partial h^*}{\partial H}\right)_{T,\,p} = H\left[T\left(\frac{\partial \chi}{\partial T}\right)_{H,\,p} - \chi\right]. \tag{9.10}$$

The heat capacities of a magnetic substance at $H$ and $j$ constant (provided that the pressure of the surrounding medium is constant), determined, according to (5.99), by obvious relationships

$$c_{H,p}=T\left(\frac{\partial s}{\partial T}\right)_{H,p} \tag{9.11}$$

and

$$c_{j,p}=T\left(\frac{\partial s}{\partial T}\right)_{j,p}, \tag{9.12}$$

are related thus:

$$c_{H,p}-c_{j,p}=T\left(\frac{\partial j}{\partial T}\right)^2_{H,p}\left(\frac{\partial H}{\partial j}\right)_{T,p}, \tag{9.13}$$

or, which is the same,

$$c_{H,p}-c_{j,p}=-T\left(\frac{\partial j}{\partial T}\right)_{H,p}\left(\frac{\partial H}{\partial T}\right)_{j,p} \tag{9.14}$$

and

$$c_{H,p}-c_{j,p}=T\left(\frac{\partial H}{\partial T}\right)^2_{j,p}\left(\frac{\partial j}{\partial H}\right)_{T,p}. \tag{9.15}$$

We derived these relationships in the same way as (5.109)-(5.111).

From (9.8) it is clear that the partial derivatives in Eqs. (9.13) through (9.15) can be written as

$$\left(\frac{\partial j}{\partial T}\right)_{H,p}=H\left(\frac{\partial \chi}{\partial T}\right)_{H,p}, \tag{9.16}$$

$$\left(\frac{\partial j}{\partial H}\right)_{T,p}=\chi+H\left(\frac{\partial \chi}{\partial H}\right)_{T,p}, \tag{9.17}$$

and

$$\left(\frac{\partial H}{\partial T}\right)_{j,p}=-\frac{H}{\chi}\left(\frac{\partial \chi}{\partial T}\right)_{j,p}. \tag{9.18}$$

We can easily show that

$$\left(\frac{\partial c_{H,p}}{\partial H}\right)_{T,p}=T\left(\frac{\partial^2 j}{\partial T^2}\right)_{H,p}, \tag{9.19}$$

or, which is the same,

$$\left(\frac{\partial c_{H,p}}{\partial H}\right)_{T,p}=TH\left(\frac{\partial^2 \chi}{\partial T^2}\right)_{H,p}, \tag{9.20}$$

and that

$$\left(\frac{\partial c_{j,p}}{\partial j}\right)_{T,p}=-T\left(\frac{\partial^2 H}{\partial T^2}\right)_{j,p}, \tag{9.21}$$

or

$$\left(\frac{\partial c_{j,p}}{\partial j}\right)_{T,p}=-\frac{j}{\chi}\left[\frac{1}{\chi}\left(\frac{\partial \chi}{\partial T}\right)^2_{j,p}-\left(\frac{\partial^2 \chi}{\partial T^2}\right)_{j,p}\right]. \tag{9.22}$$

9.2.3. We know that magnetic substances in a magnetic field are characterized by the following thermodynamic effects.

(1) The *magnetocaloric effect*: the temperature of a magnetic substance changes with the strength of the external magnetic field.

(2) The *magnetostrictive effect*: the body's volume changes when the strength of the external magnetic field varies.

(3) The *magnetoelastic effect*: the magnetization changes with the external pressure.

The magnetocaloric effect is characterized by the value of $(\partial T/\partial H)$. It is evident that the value is different for different thermodynamic processes (with the change in the field strength) in which a magnetic substance is involved. Of particular interest is the magnetocaloric effect that occurs when the state of the substance is changed adiabatically; here the effect is characterized by the value of $(\partial T/\partial H)_{s,p}$ In accordance with (2.67) we can write

$$\left(\frac{\partial T}{\partial H}\right)_{s,\,p}=-\left(\frac{\partial s}{\partial H}\right)_{T,\,p}\left(\frac{\partial T}{\partial s}\right)_{H,\,p}, \tag{9.23}$$

whence, taking into account (9.7) and (9.11), we obtain

$$\left(\frac{\partial T}{\partial H}\right)_{s,\,p}=-\frac{T}{c_{H,\,p}}\left(\frac{\partial j}{\partial T}\right)_{H,\,p}, \tag{9.24}$$

or, taking into account (9.16),

$$\left(\frac{\partial T}{\partial H}\right)_{s,\,p}=-\frac{TH}{c_{H,\,p}}\left(\frac{\partial \chi}{\partial T}\right)_{H,\,p}. \tag{9.25}$$

Since $c_{H,p}$ is always positive, the sign of the adiabatic magnetocaloric effect is determined by the sign of $(\partial\chi/\partial T)_{H,p}$. The magnetostrictive effect is characterized by the value of $(\partial v/\partial H)_p$ and the magnetoelastic effect by the value of $(\partial j/\partial p)_H$. Just as the value of $(\partial T/\partial H)$ is, these values are different for different thermodynamic processes. These effects are of the greatest interest in adiabatic and isothermal conditions.

We can easily establish a relationship between the values of $(dv/dH)_p$ for adiabatic and isothermal conditions. According to (2.71) we can write

$$\left(\frac{\partial v}{\partial H}\right)_{s,\,p}=\left(\frac{\partial v}{\partial H}\right)_{T,\,p}+\left(\frac{\partial v}{\partial T}\right)_{H,\,p}\left(\frac{\partial T}{\partial H}\right)_{s,\,p}. \tag{9.26}$$

In the same way we can write a relation connecting the values of $(\partial j/\partial p)_H$ for adiabatic and isothermal conditions:

$$\left(\frac{\partial j}{\partial p}\right)_{s,\,H}=\left(\frac{\partial j}{\partial p}\right)_{T,\,H}+\left(\frac{\partial j}{\partial T}\right)_{p,\,H}\left(\frac{\partial T}{\partial p}\right)_{s,\,H}. \tag{9.27}$$

Thermodynamics enables us to establish a one-to-one relationship between the magnetostrictive and magnetoelastic effects. For the systems under consideration (magnetic substances in a magnetic field), Eqs. (3.68a)

$$\left(\frac{\partial h^*}{\partial p}\right)_{T,\,\xi}=v$$

and (3.69a)

$$\left(\frac{\partial h^*}{\partial \xi}\right)_{T,\,p}=w$$

will be written, respectively, as

$$\left(\frac{\partial h^*}{\partial p}\right)_{T,\,H}=v \tag{9.28}$$

and

$$\left(\frac{\partial h^*}{\partial H}\right)_{T,\,p}=-j \tag{9.29}$$

where $h^*$ is the enthalpy of a magnetic substance determined by (9.3).

According to (2.12) and (2.13), it follows from (9.28) and (9.29) that

$$\left(\frac{\partial v}{\partial H}\right)_{s,\,p}=-\left(\frac{\partial j}{\partial p}\right)_{s,\,H}. \tag{9.30}$$

In a similar manner, Eqs. (3.76a)

$$\left(\frac{\partial \varphi^*}{\partial p}\right)_{s,\,\xi}=v$$

and (3.77a)

$$\left(\frac{\partial \varphi^*}{\partial \xi}\right)_{s,\,p}=w$$

for the systems under consideration can be written as

$$\left(\frac{\partial \varphi^*}{\partial p}\right)_{s,\,H}=v \tag{9.31}$$

and

$$\left(\frac{\partial \varphi^*}{\partial H}\right)_{s,\,p}=-j, \tag{9.32}$$

where

$$\varphi^*=u+pv-Hj-Ts \tag{9.33}$$

is the chemical potential of the magnetic substance (see (3.59a)).

In accordance with (2.12) and (2.13), from (9.31) and (9.32) we obtain

$$\left(\frac{\partial v}{\partial H}\right)_{T,\,p}=-\left(\frac{\partial j}{\partial p}\right)_{T,\,H}. \tag{9.34}$$

Equations (9.30) and (9.34) enable us, for one, to calculate the variation in the volume of a magnetic substance with magnetostriction as follows:

$$v(s,\ p,\ H)-v(s,\ p,\ H=0)=\int\limits_0^H\left(\frac{\partial v}{\partial H}\right)_{s,\ p}dH \qquad (9.35)$$

and

$$v(T,\ p,\ H)-v(T,\ p,\ H=0)=\int\limits_0^H\left(\frac{\partial v}{\partial H}\right)_{T,\ p}dH. \qquad (9.36)$$

From (9.8) it follows that

$$\left(\frac{\partial j}{\partial p}\right)_H=H\left(\frac{\partial \chi}{\partial p}\right)_H. \qquad (9.37)$$

Taking into account (9.34) and (9.37) and bearing in mind that the value of $(\partial x/\partial p)_H$ can be regarded for all practical purposes independent of $H$, from (9.35) and (9.36) we obtain

$$v(s,\ p,\ H)-v(s,\ p,\ H=0)=-\frac{H^2}{2}\left(\frac{\partial \chi}{\partial p}\right)_{s,\ H} \qquad (9.38)$$

and

$$v(T,\ p,\ H)-v(T,\ p,\ H=0)=-\frac{H^2}{2}\left(\frac{\partial \chi}{\partial p}\right)_{T,\ H}. \qquad (9.39)$$

Similarly, we can easily obtain the relations determining the variation in $j$ with the magnetoelastic effect (the change in the external pressure from $p$ to $p+\Delta p$). From the obvious relations

$$j(s,\ p+\Delta p,\ H)-j(s,\ p,\ H)=\int\limits_p^{p+\Delta p}\left(\frac{\partial j}{\partial p}\right)_{s,\ H}dp \qquad (9.40)$$

and

$$j(T,\ p+\Delta p,\ H)-j(T,\ p,\ H)=\int\limits_p^{p+\Delta p}\left(\frac{\partial j}{\partial p}\right)_{T,\ H}dp, \qquad (9.41)$$

taking into account (9.37) and the fact that usually $(\partial\chi/\partial p)_H$ changes little with pressure, we find that

$$j(s,\ p+\Delta p,\ H)-j(s,\ p,\ H)=H\left(\frac{\partial \chi}{\partial p}\right)_{s,\ H}\Delta p \qquad (9.42)$$

and

$$j(T,\ p+\Delta p,\ H)-j(T,\ p,\ H)=H\left(\frac{\partial \chi}{\partial p}\right)_{T,\ H}\Delta p. \qquad (9.43)$$

9.2.4. Superconductors are a special variety of magnetic substances. In Sec. 7.2 we noted that the mass specific magnetization of a superconductor in the superconducting state is given by Eq. (7.30)

$$j_{\text{super}} = -v_{\text{super}} H_{\text{cr}}/4\pi,$$

where $v_{\text{super}}$ is the specific volume of a superconductor in the superconducting state and $H_{\text{cr}}$ is its critical magnetic field, and its specific magnetization in the normal state, $j_{\text{norm}}$, is negligible as compared with $j_{\text{super}}$ (i.e.' superconductors in the normal state are practically nonmagnetic). In other words, for superconductors

$$\chi_{\text{super}} = -v_{\text{super}}/4\pi \tag{9.44}$$

and (9.45)

$$\chi_{\text{norm}} = 0.$$

In Sec. 7.2 we discussed the Keesom equation (7.31) for the phase transition curve of a superconductor from the superconducting state to the normal:

$$\frac{dH_{\text{cr}}}{dT} = -\frac{4\pi q}{T v_{\text{super}} H_{\text{cr}}},$$

where $q$ is the heat of this phase transition.

The relation that connects the values of the heat capacities $c_{H,p}$ of a superconductor in the superconducting and normal states on the phase transition line is important for the thermodynamics of superconductors (for the phase transition in a superconductor this relation plays the same role as the Planck equation (7.223) for the liquid-vapor phase transition).

According to (7.25), we can write for the phase transition of the superconductor

$$s_{\text{norm}} - s_{\text{super}} = q/T. \tag{9.46}$$

If we take the total derivatives of the left and right sides of (9.46) with respect to temperature along the line of phase transition, we obtain

$$\frac{ds_{\text{norm}}}{dT} - \frac{ds_{\text{super}}}{dT} = \frac{1}{T}\left(\frac{dq}{dT} - \frac{q}{T}\right). \tag{9.47}$$

Next, in accordance with (6.4) and (6.5), we can write

$$\frac{ds_{\text{norm}}}{dT} = \left(\frac{\partial s}{\partial T}\right)^{\text{norm}}_{H,\,p} + \left(\frac{\partial s}{\partial H}\right)^{\text{norm}}_{H,\,p} \frac{dH_{\text{cr}}}{dT} \tag{9.48}$$

and

$$\frac{ds_{\text{super}}}{dT} = \left(\frac{\partial s}{\partial T}\right)^{\text{super}}_{H,\,p} + \left(\frac{\partial s}{\partial H}\right)^{\text{super}}_{T,\,p} \frac{dH_{\text{cr}}}{dT}, \tag{9.49}$$

or, taking into account (9.11) and (9.7),

$$\frac{ds_{\text{norm}}}{dT}=\frac{c_{H,\,p}^{\text{norm}}}{T}+\left(\frac{\partial\chi_{\text{norm}}}{\partial T}\right)_{H,\,p}\frac{dH_{\text{cr}}}{dT} \tag{9.50}$$

and

$$\frac{ds_{\text{super}}}{dT}=\frac{c_{H,\,p}^{\text{super}}}{T}+\left(\frac{\partial\chi_{\text{super}}}{\partial T}\right)_{H,\,p}\frac{dH_{\text{cr}}}{dT}. \tag{9.51}$$

Using (9.50) and (9.51), from (9.47) we obtain

$$c_{H,\,p}^{\text{super}}-c_{H,\,p}^{\text{norm}}=\frac{q}{T}-\frac{dq}{dT}-T\left[\left(\frac{\partial\chi_{\text{super}}}{\partial T}\right)_{H,\,p}-\left(\frac{\partial\chi_{\text{norm}}}{\partial T}\right)_{H,\,p}\right]\frac{dH_{\text{cr}}}{dT}. \tag{9.52}$$

Combining this with (9.8), we find that

$$c_{H,\,p}^{\text{super}}-c_{H,\,p}^{\text{norm}}=\frac{q}{T}-\frac{dq}{dT}-TH\left[\left(\frac{\partial\chi_{\text{super}}}{\partial T}\right)_{H,\,p}-\left(\frac{\partial\chi_{\text{norm}}}{\partial T}\right)_{H,\,p}\right]\frac{dH_{\text{cr}}}{dT}. \tag{9.53}$$

Taking into account (9.44) and (9.45), we can transform this relation to

$$c_{H,\,p}^{\text{super}}-c_{H,\,p}^{\text{norm}}=\frac{q}{T}-\frac{dq}{dT}+\frac{TH}{4\pi}\left(\frac{\partial v_{\text{super}}}{\partial T}\right)_{H,\,p}. \tag{9.54}$$

Since we can assume with a high degree of accuracy that $(\partial v_{\text{super}}/\partial T)_{H,p}\approx 0$ at the transition temperature,[2] we can write Eq. (9.54) as

$$c_{H,\,p}^{\text{super}}-c_{H,\,p}^{\text{norm}}=\frac{q}{T}-\frac{dq}{dT}. \tag{9.55}$$

Next, from (7.31) we see that the heat of phase transition of a superconductor from the superconducting to the normal state is

$$q=-\frac{v_{\text{super}}TH}{4\pi}\frac{dH_{\text{cr}}}{dt}. \tag{9.56}$$

Combining this with (9.55), we obtain

$$c_{H,\,p}^{\text{super}}-c_{H,\,p}^{\text{norm}}=\frac{v_{\text{super}}T}{4\pi}\left[\left(\frac{dH_{\text{cr}}}{dT}\right)^2+\frac{H}{v_{\text{super}}}\frac{dv_{\text{super}}}{dT}\frac{dH_{\text{cr}}}{dT}+H\frac{d^2H_{\text{cr}}}{dT^2}\right], \tag{9.57}$$

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[2] In this connection we recall that, in accordance with the Nernst heat theorem, the derivative $(\partial v/\partial T)_T$ decreases as we approach absolute zero and

$$\lim_{T\to 0K}\left(\frac{\partial v}{\partial T}\right)_p=0.$$

or, bearing in mind that at the temperature of transition from the superconducting to the normal state $dv_{\text{super}}/dt \approx 0$,

$$c_{H,p}^{\text{super}} - c_{H,p}^{\text{norm}} = \frac{v_{\text{super}}T}{4\pi}\left[\left(\frac{dH_{\text{cr}}}{dT}\right)^2 + H\frac{d^2H_{\text{cr}}}{dT^2}\right]. \tag{9.58}$$

This is the relation connecting the values of $c_{H,p}$ in the superconducting and normal phases on the phase transition curve.

For the phase transition in a superconductor in the absence of an external magnetic field ($H = 0$), Eq. (9.58) assumes the form:

$$c_{H,p}^{\text{super}} - c_{H,p}^{\text{norm}} = \frac{v_{\text{super}}T}{4\pi}\left(\frac{dH_{\text{cr}}}{dT}\right)^2. \tag{9.59}$$

We discussed this relation (known as the Rutger] equation) in Sec. 7.9, Eq. (7.300), where we obtained it in a different way, as a particular case of the Ehrenfest equation (7.290) for the second-order phase transition (we recall that the phase transition of a superconductor from the superconducting to the normal state at $H = 0$ degenerates into a second-order phase transition).

Equations (9.38) and (9.39) combined with (9.44) and (9.45) enable us to calculate the variation in volume of a superconductor with magnetostriction. These relations yield, first,

$$v_{\text{super}}(s, p, H) - v_{\text{super}}(s, p, H=0) = \frac{H^2}{8\pi}\left(\frac{\partial v_{\text{super}}}{\partial p}\right)_{s,H} \tag{9.60}$$

and

$$v_{\text{super}}(T, p, H) - v_{\text{super}}(T, p, H=0) = \frac{H^2}{8\pi}\left(\frac{\partial v_{\text{super}}}{\partial p}\right)_{T,H}. \tag{9.61}$$

Since $(\partial v/\partial p)_s$ and $(\partial v/\partial p)_T$ are always negative, the volume of a superconductor in the superconducting state decreases as the strength of the external magnetic field grows. Next, since according to (5.122) the adiabatic compressibility is less than the isothermal compressibility, the volume of a superconductor in the superconducting state, as $H$ increases by one and the same value, decreases more in isothermal conditions than in adiabatic. Second, since according to (9.45) a superconductor in the normal state is nonmagnetic, the magnetostrictive effect here is zero.

Similarly, if we combine (9.42) and (9.43) with (9.44), we see that for a superconductor in the superconducting state the variation in the specific magnetization due to the magnetoelastic effect is given thus:

$$j_{\text{super}}(s, p+\Delta p, H) - j_{\text{super}}(s, p, H) = -\frac{H}{4\pi}\left(\frac{\partial v_{\text{super}}}{\partial p}\right)_{s,H}\Delta p \tag{9.62}$$

and

$$j_{\text{super}}(T,\ p+\Delta p,\ H)-j_{\text{super}}(T,\ p,\ H)$$
$$=-\frac{H}{4\pi}\left(\frac{\partial v_{\text{super}}}{\partial p}\right)_{T,\ H}\Delta p. \tag{9.63}$$

For reasons similar to those given above it follows that, first, the magnetization of a superconductor in the superconducting state increases with pressure and, second, this effect is greater in absolute value in isothermal conditions than in adiabatic. From (9.42) and (9.43), taking into account (9.45), we see that a superconductor in the normal state has no magnetoelastic effect.

## 9.3 Systems in an Electric Field

9.3.1. We know that for a dielectric in an electric field the electric field strength taken with the minus sign, $-E$, is the generalized force, $\xi$, and the polarization of the dielectric, $\mathfrak{P}$, is the generalized coordinate, $W$.

Hence, the combined equation of the first and second laws of thermodynamics (Eq. (1.30)) for such a system is

$$T\,dS = dU + p\,dV - E\,d\mathfrak{P}, \tag{9.64}$$

and for volume specific quantities

$$T\,ds_v = du_v + p\,\frac{dV}{V} - E\,dP, \tag{9.65}$$

where $s_v = S/V_0$, $u_v = U/V_0$ and $P = \mathfrak{P}/V_0$, and $V_0$ is the volume of the dielectric at certain fixed parameters $T_0$, $p_0$, and $E_0$.

If we use the Legendre transformation (3.48), we can write (9.64) and (9.65) as

$$T\,dS = dH^* - V\,dp + \mathfrak{P}dE \tag{9.66}$$

and

$$T\,ds_v = dh_v^* - \frac{Vdp}{V_0} + P\,dE, \tag{9.67}$$

where

$$H^* = U + pV - E\mathfrak{P} \tag{9.68}$$

and

$$h_v^* = u_v + p - EP \tag{9.69}$$

are the total enthalpy and the volume specific enthalpy, respectively, of the system in an electric field.

Equations (4.17c), (4.20b), (4.23c), and (4.26b) for the whole system assume the form

$$\left(\frac{\partial \mathfrak{P}}{\partial T}\right)_{S,\,V}=\left(\frac{\partial S}{\partial E}\right)_{\mathfrak{P},\,V}, \tag{9.70}$$

$$\left(\frac{\partial \mathfrak{P}}{\partial S}\right)_{E,\,p}=-\left(\frac{\partial T}{\partial E}\right)_{S,\,p}, \tag{9.71}$$

$$\left(\frac{\partial \mathfrak{P}}{\partial S}\right)_{T,\,V}=-\left(\frac{\partial T}{\partial E}\right)_{\mathfrak{P},\,V}, \tag{9.72}$$

$$\left(\frac{\partial \mathfrak{P}}{\partial T}\right)_{E,\,p}=\left(\frac{\partial S}{\partial E}\right)_{T,\,p}. \tag{9.73}$$

For volume specific quantities the Maxwell equations have the same form except that $\mathfrak{P}$ and $S$ are replaced by $P$ and $s_v$.

We know that the polarization of a dielectric (the electric dipole moment per unit volume of the dielectric), $P$, is related to the electric field strength $E$ by

$$P=\alpha E, \tag{9.74}$$

where $\alpha$ is known as the *electric* or *dielectric*, *susceptibility*. This relationship can obviously be regarded as the equation of state for a dielectric in an electric field. It is common practice in calculating dielectrics to write the dielectric susceptibility $\alpha$ as

$$\alpha=(\varepsilon-1)/4\pi, \tag{9.75}$$

where $\varepsilon$ is called the permittivity of the dielectric, and, hence, the equation of state (9.74), is written thus

$$P=\frac{\varepsilon-1}{4\pi}E. \tag{9.76}$$

In calculating the generalized coordinate, magnetization $j$, of magnetic substances, discussed in the previous section, it is common to use mass specific quantities, while in calculating dielectrics the practice is to write the generalized coordinate, polarization $P$, in terms of volume specific quantities. In view of this we employ volume specific values of enthalpy, entropy, and other thermodynamic quantities.

9.3.2. If we combine (9.65) with (9.72) written for volume specific quantities and (9.76), we obtain

$$\left(\frac{\partial u_v}{\partial P}\right)_{T,\,V}=E\left[1+\frac{T}{\varepsilon-1}\left(\frac{\partial \varepsilon}{\partial T}\right)_{P,\,V}\right]. \tag{9.77}$$

Similarly, combining (9.67) with (9.73) written for volume specific quantities and (9.76), we find that

$$\left(\frac{\partial h_v^*}{\partial P}\right)_{T,\,p}=\frac{E}{4\pi}\left[T\left(\frac{\partial \varepsilon}{\partial T}\right)_{E,\,p}-\varepsilon+1\right]. \tag{9.78}$$

In accordance with (5.99), the volume heat capacities of a dielectric at $E$ and $P$ constant are determined in the obvious way:

$$C_{E,\,p}=T\left(\frac{\partial s_v}{\partial T}\right)_{E,\,p} \tag{9.79}$$

and

$$C_{P,\,p}=T\left(\frac{\partial s_v}{\partial T}\right)_{P,\,p}. \tag{9.80}$$

By the same method as we used for deriving Eqs. (5.109) through (5.111), we can easily show that

$$C_{E,\,p}-C_{P,\,p}=T\left(\frac{\partial P}{\partial T}\right)^2_{E,\,p}\left(\frac{\partial E}{\partial P}\right)_{T,\,p}, \tag{9.81}$$

or

$$C_{E,\,p}-C_{P,\,p}=-T\left(\frac{\partial P}{\partial T}\right)_{E,\,p}\left(\frac{\partial E}{\partial T}\right)_{P,\,p}, \tag{9.82}$$

or that

$$C_{E,\,p}-C_{P,\,p}=T\left(\frac{\partial E}{\partial T}\right)^2_{P,\,p}\left(\frac{\partial P}{\partial E}\right)_{T,\,p}. \tag{9.83}$$

From (9.76) it follows that we can write the partial derivatives on the right-hand sides of Eqs. (9.81) through (9.83) as

$$\left(\frac{\partial P}{\partial T}\right)_{E,\,p}=\frac{E}{4\pi}\left(\frac{\partial \varepsilon}{\partial T}\right)_{E,\,p}, \tag{9.84}$$

$$\left(\frac{\partial P}{\partial E}\right)_{T,\,p}=\frac{1}{4\pi}\left[E\left(\frac{\partial \varepsilon}{\partial E}\right)_{T,\,p}+\varepsilon-1\right], \tag{9.85}$$

and

$$\left(\frac{\partial E}{\partial T}\right)_{P,\,p}=-\frac{E}{\varepsilon-1}\left(\frac{\partial \varepsilon}{\partial T}\right)_{P,\,p}. \tag{9.86}$$

From (9.79), using (2.13) and (9.73), we easily obtain

$$\left(\frac{\partial C_{E,\,p}}{\partial E}\right)_{T,\,p}=T\left(\frac{\partial^2 P}{\partial T^2}\right)_{E,\,p}, \tag{9.87}$$

or, which is the same,

$$\left(\frac{\partial C_{E,\,p}}{\partial E}\right)_{T,\,p}=\frac{TE}{4\pi}\left(\frac{\partial^2 \varepsilon}{\partial T^2}\right)_{E,\,p}. \tag{9.88}$$

Similarly, we can show that

$$\left(\frac{\partial C_{P,\,p}}{\partial P}\right)_{T,\,p}=-T\left(\frac{\partial^2 E}{\partial T^2}\right)_{P,\,p}, \tag{9.89}$$

or

$$\left(\frac{\partial C_{P,\,p}}{\partial P}\right)_{T,\,p}=\frac{4\pi P}{(\varepsilon-1)^2}\left[\frac{1}{\varepsilon-1}\left(\frac{\partial \varepsilon}{\partial T}\right)^2_{P,\,p}-\left(\frac{\partial^2 \varepsilon}{\partial T^2}\right)_{P,\,p}\right]. \tag{9.90}$$

9.3.3. We know that dielectrics in an electric field are characterized by the following thermodynamic effects.

(1) The *piezoelectric effect*: the variation of the polarization of a dielectric with the external pressure.

(2) The *electrostrictive effect*: the variation of the volume of a dielectric with the electric field strength. In a certain sense this effect is the opposite of the piezoelectric effect.

(3) The *pyroelectric effect*: the change in the polarization of a dielectric when its temperature changes.

(4) The *electrocaloric effect*: the change in the temperature of a dielectric when the electric field strength changes. This effect is the opposite of the pyroelectric effect.

The piezoelectric effect is characterized by the value of the derivative $(\partial\mathfrak{P}/\partial p)_E$ and the electrostrictive effect by the value of the derivative $(\partial V/\partial E)_p$. It is clear that each derivative will be different for different thermodynamic processes. An examination of these effects in adiabatic and isothermal conditions is of the most practical interest.

Equations relating the values of $(\partial\mathfrak{P}/\partial p)_E$ for adiabatic and isothermal conditions, according to (2.71), can be written as

$$\left(\frac{\partial\mathfrak{P}}{\partial p}\right)_{S,E}=\left(\frac{\partial\mathfrak{P}}{\partial p}\right)_{T,E}+\left(\frac{\partial\mathfrak{P}}{\partial T}\right)_{p,E}\left(\frac{\partial T}{\partial p}\right)_{S,E}. \tag{9.91}$$

In a similar way we can easily obtain an equation relating the values of $(\partial V/\partial E)_p$ for adiabatic and isothermal conditions:

$$\left(\frac{\partial V}{\partial E}\right)_{S,p}=\left(\frac{\partial V}{\partial E}\right)_{T,p}+\left(\frac{\partial V}{\partial T}\right)_{E,p}\left(\frac{\partial T}{\partial E}\right)_{S,p}. \tag{9.92}$$

It is obvious from general thermodynamic reasoning that there is a unique relation between the piezoelectric and electrostrictive effects. We can obtain this relation in the following way. For the system under consideration relations (3.68)

$$\left(\frac{\partial H^*}{\partial p}\right)_{T,\xi}=V$$

and (3.69)

$$\left(\frac{\partial H^*}{\partial \xi}\right)_{T,p}=W$$

can be written as

$$\left(\frac{\partial H^*}{\partial p}\right)_{T,E}=V \tag{9.93}$$

and

$$\left(\frac{\partial H^*}{\partial E}\right)_{T,p}=-\mathfrak{P}, \tag{9.94}$$

where the enthalpy of a dielectric, $H^*$, is determined by (9.68).

In accordance with (2.12) and (2.13), it follows from (9.93) and (9.94) that

$$\left(\frac{\partial V}{\partial E}\right)_{S,\,p}=-\left(\frac{\partial \mathfrak{P}}{\partial p}\right)_{S,\,E}. \tag{9.95}$$

Similarly, from (3.76)

$$\left(\frac{\partial \Phi^*}{\partial p}\right)_{S,\,\xi}=V$$

and (3.77)

$$\left(\frac{\partial \Phi^*}{\partial \xi}\right)_{S,\,p}=W,$$

which we can write for a given system as

$$\left(\frac{\partial \Phi^*}{\partial p}\right)_{S,\,E}=V \tag{9.96}$$

and

$$\left(\frac{\partial \Phi^*}{\partial E}\right)_{S,\,p}=-\mathfrak{P}, \tag{9.97}$$

where, according to (3.59a),

$$\Phi^* = U + pV - E\mathfrak{P} - TS \tag{9.98}$$

is the isobaric-isothermal potential of the system, using (2.12) and (2.13), we obtain

$$\left(\frac{\partial V}{\partial E}\right)_{T,\,p}=-\left(\frac{\partial \mathfrak{P}}{\partial p}\right)_{T,\,E}. \tag{9.99}$$

Next, we see that the pyroelectric effect is characterized by the derivative $(\partial P/\partial T)_{E,p}$, while the opposite electrocaloric effect by the derivative $(\partial T/\partial E)_p$. In principle the electrocaloric effect occurs in any thermodynamic process involving a dielectric (not an isothermal process obviously); but the adiabatic processes, characterized by $(\partial T/\partial E)_{S,p}$, are the most interesting from the practical standpoint.

From (2.67) we see that

$$\left(\frac{\partial T}{\partial E}\right)_{s_v,\,p}=-\left(\frac{\partial T}{\partial s_v}\right)_{E,\,p}\left(\frac{\partial s_v}{\partial E}\right)_{T,\,p}. \tag{9.100}$$

Taking into account (9.73) written for the volume specific quantities and (9.79), we find that

$$\left(\frac{\partial T}{\partial E}\right)_{s_v,\,p}=-\frac{T}{c_{E,\,p}}\left(\frac{\partial P}{\partial T}\right)_{E,\,p}. \tag{9.101}$$

This equation relates the magnitudes of the electrocaloric and pyroelectric effects.

9.3.4. An important particular case of a thermodynamic system involving a dielectric in an electric field is the electrical capacitor. We will not discuss in detail the thermodynamics of an electrical capacitor, but will only give some initial informations.

For a thermodynamic system that includes a capacitor and an electric field, the voltage across the plates, $V$, is the generalized force, $\xi$, and the electric charge, $Z$, is the generalized coordinate, $W$. The combined equation of the first and second laws of thermodynamics (1.30) for this system can be written as

$$T\,dS = dU + p\,dV - V dZ, \tag{9.102}$$

while the set of the Maxwell equations is

$$\left(\frac{\partial Z}{\partial T}\right)_{S,\,V} = \left(\frac{\partial S}{\partial V}\right)_{Z,\,V}, \tag{9.103}$$

$$\left(\frac{\partial Z}{\partial S}\right)_{\mathfrak{W},\,p} = -\left(\frac{\partial T}{\partial V}\right)_{S,\,p}, \tag{9.104}$$

$$\left(\frac{\partial Z}{\partial S}\right)_{T,\,V} = -\left(\frac{\partial T}{\partial V}\right)_{Z,\,V}, \tag{9.105}$$

$$\left(\frac{\partial Z}{\partial Z}\right)_{\mathfrak{W},\,p} = \left(\frac{\partial S}{\partial V}\right)_{T,\,p}. \tag{9.106}$$

Finally, the equation of state of such a system, namely, the equation relating the electric charge on a capacitor plate, $Z$, and the voltage across the plates, $V$, has as we know from electrostatics, the following form:

$$Z = \mathfrak{C}V \tag{9.107}$$

where $\mathfrak{C}$ is the capacitance of the capacitor.

These are the main aspects of a thermodynamic description of the electrical capacitor.

## 9.4 Systems in a Gravitational Field

9.4.1. The elementary work performed in lifting a body of mass $G$ to a height $dz$ in a gravitational field is

$$dL^* = gG dz, \tag{9.108}$$

where $g$ is the acceleration of gravity. Hence, for a system in a gravitational field the weight $gG$ is the generalized force, $\xi$, and the height of the center of gravity of the system, $z$, is the generalized coordinate, $W$. Therefore, in accordance with (1.30), the combined equation of the first and second laws of thermodynamics for a system in a gravitational field can be written as

$$T\,dS = dU + p\,dV + gG dz, \tag{9.109}$$

or for mass specific quantities (if the mass $G$ of the system remains constant)

$$T\,ds = du + p\,dv + gdz. \tag{9.110}$$

9.4.2. Interestingly, for a system in a gravitational field, as we can see from (9.109), the weight $gG$ of the body in contrast to other known generalized forces is an extensive rather than intensive quantity. The generalized coordinate, height $z$, however, is not extensive but intensive. In this connection we note that Eq. (9.109) can be transformed to a form more "common" from the point of view of the intensity and capacity factors. To this end we use the Legendre transformation

$$Gdz = d\,(Gz) - zdG, \tag{9.111}$$

and from (9.109) find that

$$T\,dS = d\,(U + gGz) + p\,dV - gzdG. \tag{9.112}$$

The sum $U + gGz$ in this equation can be interpreted as the "total" energy of the system:

$$U^* = U + gGz, \tag{9.113}$$

by analogy with the total enthalpy of such a system defined in the general case by Eq. (1.15). The enthalpy $H^*$ of the entire system is

$$H^* = U + pV + gGz. \tag{9.114}$$

If we combine the Legendre transformation (3.4) with (9.114), from (9.112) we obtain

$$T\,dS = dH^* - V\,dp - gzdG. \tag{9.115}$$

These are the basic relations for thermodynamic systems in a gravitational field.

## 9.5 Elastically Deformed Systems

9.5.1. We consider a solid (a rod) which is elastically deformed under a tensile (or compressive) force $\Psi$. Here $\Psi$ is the generalized force, $\xi$, and the length of the rod, $l$, is the generalized coordinate, $W$. Hence, the combined equation of the first and second laws of thermodynamics (Eq. (1.30)) for such a system is written as

$$T\,dS = dU + p\,dV - \Psi\,dl. \tag{9.116}$$

Since under tension the rod's volume usually changes very slightly (as we will see later), for most cases of practical importance we may assume to a good approximation that $V$ is constant and write (9.116) as

$$T\,dS = dU - \Psi\,dl. \tag{9.117}$$

In accordance with (4.17c), (4.20b), (4.23c), and (4.26b), for an elastically deformed rod the Maxwell equations (with either $p$ or $V$ kept constant) are as follows:

$$\left(\frac{\partial l}{\partial T}\right)_{S,\,V}=\left(\frac{\partial S}{\partial \Psi}\right)_{l,\,V}, \tag{9.118}$$

$$\left(\frac{\partial l}{\partial S}\right)_{\Psi,\,p}=-\left(\frac{\partial T}{\partial \Psi}\right)_{S,\,p}, \tag{9.119}$$

$$\left(\frac{\partial l}{\partial S}\right)_{T,\,V}=-\left(\frac{\partial T}{\partial \Psi}\right)_{l,\,V}, \tag{9.120}$$

$$\left(\frac{\partial l}{\partial T}\right)_{\Psi,\,p}=\left(\frac{\partial S}{\partial \Psi}\right)_{T,\,p}. \tag{9.121}$$

It is evident that the magnitude of the tensile (or compressive) force on the rod can be expressed as

$$\Psi = \psi\Omega, \tag{9.122}$$

where $\Omega$ is the cross-sectional area of the rod, and $\psi$ is the tensile force per unit cross-sectional area, or stress. In practice the change in the size of the solid under stress is expressed in terms of the relative change in length, or strain, $\varepsilon$, as

$$\varepsilon = (l - l_0)/l_0, \tag{9.123}$$

where $l_0$ is the length of the rod in the absence of a load, and $l$ is the length of the rod under a load. From (9.123) we see that

$$dl = l_0\, d\varepsilon + (1+\varepsilon)\, dl_0 \tag{9.124}$$

($l_0$ changes with temperature).

Taking into account (9.122) and (9.124), we can write (9.117) as

$$T\,dS = dU - \psi V_0\left(d\varepsilon + (1+\varepsilon)\frac{dl_0}{l_0}\right), \tag{9.125}$$

where $V_0 = \Omega l_0$ is the volume of the rod prior to deformation. This can be transformed to

$$T\,ds_v = du_v - \psi\,(d\varepsilon + (1+\varepsilon) d \ln l_0), \tag{9.126}$$

where $s_v$ and $u_v$ are the volume specific entropy and internal energy at a fixed temperature.

The equation of state for an elastically deformed rod widely used in the theory of elasticity is the well-known *Hooke's law*, which is usually written as

$$\varepsilon = \frac{1}{E}\,\psi, \tag{9.127}$$

where $E$ is the modulus of elasticity (Young's modulus).

9.5.2. If we take into account the Maxwell equation (9.120), we can write (9.117) as

$$\left(\frac{\partial U}{\partial l}\right)_{T,V}=\Psi-T\left(\frac{\partial \Psi}{\partial T}\right)_{l,v}. \tag{9.128}$$

Combining this with (9.122), (9.123), and, (9.127), we obtain

$$\left(\frac{\partial U}{\partial l}\right)_{T,V}=\Omega\left[\left(E-T\frac{dE}{dT}\right)\varepsilon+\frac{ET}{l_0}\alpha_l l\right], \tag{9.129}$$

where

$$\alpha_l=\frac{1}{l_0}\left(\frac{\partial l_0}{\partial T}\right) \tag{9.130}$$

is the linear thermal expansion coefficient of the material of the rod.

In a similar way we can obtain a relation for the dependence of the enthalpy $H^*$ of the deformed rod on the force $\Psi$. In accordance with Eq. (1.15), the enthalpy of the system under consideration can be written as

$$H^*=H+pV-\Psi\,(l-l_0). \tag{9.131}$$

We must note that for $W$ in (1.15) we take not the length of the rod $l$, but the difference $l-l_0$, which is the change in the rod's length under the force $\Psi$; the physical meaning of this remark is obvious.

9.5.3. The process of rod deformation is accompanied by changes in the temperature of the rod, i.e. the *elastocaloric effect*. Of the most interest from the practical standpoint is the evaluation of the elastocaloric effect when the rod is deformed adiabatically (the adiabatic elastocaloric effect is sometimes called the *Joule effect*). It is evident that the adiabatic elastocaloric effect is characterized by the derivative $(dT/\partial\Psi)_{S,p}$.

To calculate $(\partial T/\partial\Psi)_{S,p}$, we use the Maxwell equation (9.119)

$$\left(\frac{\partial T}{\partial \Psi}\right)_{S,p}=-\left(\frac{\partial l}{\partial S}\right)_{\Psi,p}. \tag{9.132}$$

In accordance with (2.6) we can write

$$\left(\frac{\partial l}{\partial S}\right)_{\Psi,p}=\left(\frac{\partial l}{\partial T}\right)_{\Psi,p}\left(\frac{\partial T}{\partial S}\right)_{\Psi,p}. \tag{9.133}$$

We see further that

$$\left(\frac{\partial T}{\partial S}\right)_{\Psi,p}=\frac{T}{c_{\psi,p}G}, \tag{9.134}$$

where

$$c_{\psi,p}=T\left(\frac{\partial s}{\partial T}\right)_{\psi,p} \tag{9.135}$$

is the specific heat capacity of the material at constant stress (this value practically coincides with the constant-pressure heat capacity $c_p$), and $G$ is the mass of the rod.

If we combine (9.130), (9.133), and (9.134) with (9.132), we obtain

$$\left(\frac{\partial T}{\partial \Psi}\right)_{S,\,p} = -\frac{\alpha l_0 T}{c_p G}. \tag{9.136}$$

This relation enables us to calculate the change in temperature due to the elastocaloric effect.

9.5.4. We can account for the change in the volume of an elastic rod as follows. We can show that at constant temperature the change in the volume of the rod with its length is determined by

$$\frac{dV}{V_0} = (1-2\mu)\, d\varepsilon, \tag{9.137}$$

where $\mu$ is known as the *Poisson ratio* and is defined by the ratio $\varepsilon_1/\varepsilon$, where $\varepsilon$ is the relative longitudinal deformation (see (9.123)), and $\varepsilon_1$ is the relative transverse deformation of the rod.

If we use (9.137), we can write (9.116) as

$$T\, dS = dU + V_0\, [(1-2\mu)\, p - \psi]\, d\varepsilon, \tag{9.138}$$

or in volume specific quantities

$$T\, ds_v = du_v + [(1-2\mu)\, p - \psi]\, d\varepsilon. \tag{9.139}$$

Unlike (9.117) and (9.126), these relations account for the change in the volume of an elastic rod at constant temperature. The reader can easily find the relations for a varying temperature.

9.5.5. Aside from problems concerning longitudinal deformation of an elastic rod, it is interesting in some cases to consider an elastic rod subjected to a certain torque $\mathfrak{M}$. For such a thermodynamic system the torque $\mathfrak{M}$ is the generalized force, $\xi$, and the angle $\omega$ through which the rod is twisted by the torque $\mathfrak{M}$ in the generalized coordinate $W$. The combined equation of the first and second laws of thermodynamics (1.30) is then written as

$$T\, dS = dU + p\, dV - \mathfrak{M} d_{\omega}. \tag{9.140}$$

A detailed thermodynamic analysis of torsion in a rod can be done in a way similar to that for a stretched (or compressed) rod; in the corresponding differential equations we must replace $\Psi$ by $\mathfrak{M}$ and $l$ by $\omega$.

## 9.6 Voltaic Systems

9.6.1. We know that for a reversible voltaic cell the electromotive force, $\mathscr{E}$, is the generalized force and the electric charge, $Z$, is the generalized coordinate. Hence, the combined equation of the first and second laws of thermodynamics (1.30) is written as

$$T\,dS = dU + p\,dV - \mathcal{E}dZ. \tag{9.141}$$

If the volume of the system is kept constant (and only this case is analysed when studying the thermodynamics of a voltaic cell), this relation assumes the form

$$T\,dS = dU - \mathcal{E}dZ. \tag{9.142}$$

The Maxwell equations (4.17c), (4.20c), (4.23b), and (4.26b) as applied to a reversible voltaic cell can be written in the following form:

$$\left(\frac{\partial Z}{\partial T}\right)_{S,\,V} = \left(\frac{\partial S}{\partial \mathcal{E}}\right)_{Z,\,V}, \tag{9.143}$$

$$\left(\frac{\partial S}{\partial Z}\right)_{\mathcal{E},\,p} = -\left(\frac{\partial \mathcal{E}}{\partial T}\right)_{S,\,p}, \tag{9.144}$$

$$\left(\frac{\partial S}{\partial Z}\right)_{T,\,V} = -\left(\frac{\partial \mathcal{E}}{\partial T}\right)_{Z,\,V}, \tag{9.145}$$

$$\left(\frac{\partial Z}{\partial T}\right)_{S,\,V} = \left(\frac{\partial S}{\partial \mathcal{E}}\right)_{T,\,p}. \tag{9.146}$$

We also know that the emf, $\mathcal{E}$, of a reversible cell is a function of temperature and does not depend on the extent to which the cell is charged. Therefore, (1) Eq. (9.146) is meaningless since if $T$ is constant so is $\mathcal{E}$ (and vice versa), and (2) Eqs. (9.144) and (9.145) are identical and can be written as

$$\left(\frac{\partial S}{\partial Z}\right)_{T,\,p,\,V} = -\frac{d\mathcal{E}}{dT}. \tag{9.147}$$

Thus, for a reversible voltaic cell the system of Maxwell equations consists of two equations only, namely Eqs. (9.143) and (9.147).

9.6.2. Next, let us examine how the internal energy $U$ of a voltaic cell changes with charge $Z$ at constant temperature. (We assume that the pressure in the system remains unchanged, $p =$ const, and the change in the volume of the system is negligible, $V =$ const.) Equation (9.142) then yields

$$\left(\frac{\partial U}{\partial Z}\right)_{T,\,V} = T\left(\frac{\partial S}{\partial Z}\right)_{T,\,V} + \mathcal{E}. \tag{9.148}$$

If we combine this with (9.147), we obtain

$$\left(\frac{\partial U}{\partial Z}\right)_{T,\,V} = \mathcal{E} - T\frac{d\mathcal{E}}{dT}. \tag{9.149}$$

After integration we arrive at a relation that enables us to determine how much the internal energy of a reversible cell changes as the charge changes by $\Delta Z = Z_2 - Z_1$ at $T = \text{const}$:

$$U_2(T, Z_2) - U_1(T, Z_1) = \int_{Z_1}^{Z_2} \left(\mathscr{E} - T\frac{d\mathscr{E}}{dT}\right) dZ. \tag{9.150}$$

Since $\mathscr{E}$ depends solely on the temperature, from (9.150) it follows that

$$U_2(T, Z_2) - U_1(T, Z_1) = \left(\mathscr{E} - T\frac{d\mathscr{E}}{dT}\right)(Z_2 - Z_1). \tag{9.151}$$

Furthermore, since in the system under consideration $p$ and $V$ are constant, from the definition of "ordinary" enthalpy (1.14)

$$H = U + pV$$

it is evident that here

$$U_2 - U_1 = H_2 - H_1 \tag{9.152}$$

and Eq. (9.151) can be expressed as

$$H_2(T, p, Z_2) - H_1(T, p, Z_1) = \left(\mathscr{E} - T\frac{d\mathscr{E}}{dT}\right)\Delta Z. \tag{9.153}$$

In this equation the difference between the enthalpies of the system in the final and initial states in a process taking place under isobaric-isothermal conditions is, according to (5.80), simply the heat of the isobaric-isothermal reaction:

$$Q_p = H_2 - H_1.$$

With this in mind, we can write Eq. (9.153) as follows:

$$Q_p = \left(\mathscr{E} - T\frac{d\mathscr{E}}{dT}\right)\Delta Z. \tag{9.154}$$

This important equation connects the heat of reaction, $Q_p$, in a voltaic cell and the cell's emf, $\mathscr{E}$. It is known as the *Helmholtz equation.*

If we compare this equation with the Gibbs-Helmholtz equation (5.82)

$$-Q_p = L^*_{p,T} - T\left(\frac{\partial L^*_{p,T}}{\partial T}\right)_p,$$

we see that the Helmholtz equation for a voltaic cell (9.154) is a particular case of (5.82).

## 9.7 Two-Dimensional Surface Systems

9.7.1. We know that the interface between two phases has special features: there is surface tension and the surface layer as a whole has excess internal energy (called surface energy). This surface layer is very thin (of the order of several monomolecular layers) and since its volume is negligible if compared with the whole bulk of the liquid, we are justified in assuming that the surface layer has zero thickness (and, hence, zero volume) and that the special features of this layer (excess energy, for one) manifest themselves only at the surface of the liquid. We will then speak of surface energy, surface heat capacity, surface entropy, etc.

9.7.2. Let us study a thermodynamic system that is an interfacial surface with no thickness. For such a system the surface area, $\mathfrak{S}$, is the generalized coordinate, $W$, and the surface tension taken with the minus sign,-$\sigma$, is the generalized force, $\xi$. The surface tension $\sigma$ is a unique function of temperature. The functional relationship $\sigma(T)$ for a given substance is the equation of state for the system under consideration.

The combined equation of the first and second laws of thermodynamics (1.30) for this two-dimensional system ($V = 0$) can be written as

$$T\,dS = dU - \sigma\,d\mathfrak{S}. \tag{9.155}$$

For the given system we can write the Maxwell equations (4.17c), (4.20b), (4.23c), and (4.26b) as

$$\left(\frac{\partial\mathfrak{S}}{\partial T}\right)_S = \left(\frac{\partial S}{\partial\sigma}\right)_{\mathfrak{S}}, \tag{9.156}$$

$$\left(\frac{\partial\mathfrak{S}}{\partial S}\right)_\sigma = -\left(\frac{\partial T}{\partial\sigma}\right)_S, \tag{9.157}$$

$$\left(\frac{\partial\mathfrak{S}}{\partial S}\right)_T = -\left(\frac{\partial T}{\partial\sigma}\right)_{\mathfrak{S}}, \tag{9.158}$$

$$\left(\frac{\partial\mathfrak{S}}{\partial T}\right)_\sigma = \left(\frac{\partial S}{\partial\sigma}\right)_T. \tag{9.159}$$

Bearing in mind that $\sigma$ is a unique function of temperature, we see that, first, Eqs. (9.157) and (9.158) are identical and can be written as

$$\left(\frac{\partial S}{\partial\mathfrak{S}}\right)_T = \left(\frac{\partial S}{\partial\mathfrak{S}}\right)_\sigma = -\frac{d\sigma}{dT}. \tag{9.160}$$

Second, it is obvious that Eqs. (9.156) and (9.159) are meaningless. Indeed, since $T$ is constant, so is $\sigma$, and the derivatives in (9.159) are zero. We easily see that the situation is the same with the derivatives in (9.156). From (2.71) it follows that

$$\left(\frac{\partial\mathfrak{S}}{\partial T}\right)_S = \left(\frac{\partial\mathfrak{S}}{\partial T}\right)_\sigma + \left(\frac{\partial\mathfrak{S}}{\partial\sigma}\right)_T \frac{d\sigma}{dT}. \tag{9.161}$$

Since $(\partial\mathfrak{S}/\partial T)_\sigma = 0$ and, of course, $(\partial\mathfrak{S}/\partial\sigma)_T = 0$, it is obvious that the derivative $(\partial\mathfrak{S}/\partial T)_S$ also equals zero.

9.7.3. The entropy, internal energy, and other caloric quantities for a surface can be written as

$$S = s_\sigma\mathfrak{S}, \tag{9.162}$$

$$U = u_\sigma\mathfrak{S}, \tag{9.163}$$

etc., where $s_\sigma$ and $u_\sigma$ are the area specific values of $S$ and $U$ (since mass and volume are meaningless concepts for a two-dimensional system, the specific quantities can only be referred to a unit area).

Next, differentiating (9.162) and (9.163) with respect to $\mathfrak{S}$ with $T$ kept constant, we obtain

$$\left(\frac{\partial S}{\partial\mathfrak{S}}\right)_T = s_\sigma + \mathfrak{S}\left(\frac{\partial s_\sigma}{\partial\mathfrak{S}}\right)_T, \tag{9.164}$$

$$\left(\frac{\partial U}{\partial\mathfrak{S}}\right)_T = u_\sigma + \mathfrak{S}\left(\frac{\partial u_\sigma}{\partial\mathfrak{S}}\right)_T. \tag{9.165}$$

Since both $s_\sigma$ and $u_\sigma$ depend only on temperature, they characterize the properties of coexisting phases (just as $\sigma$ does). Hence, we can write (9.164) and (9.165) as

$$s_\sigma = \left(\frac{\partial S}{\partial\mathfrak{S}}\right)_T, \tag{9.166}$$

$$u_\sigma = \left(\frac{\partial U}{\partial\mathfrak{S}}\right)_T. \tag{9.167}$$

The entropy $s_\sigma$ can easily be determined via Eq. (9.160): from (9.160) and (9.166) we see that

$$s_\sigma = -\frac{d\sigma}{dT}. \tag{9.168}$$

In this case the equation for the total entropy of the surface, (9.162), is

$$S = -\frac{d\sigma}{dT}\mathfrak{S}. \tag{9.169}$$

Let us now turn to $u_\sigma$. From (9.155) it follows that

$$\left(\frac{\partial U}{\partial\mathfrak{S}}\right)_T = T\left(\frac{\partial S}{\partial\mathfrak{S}}\right)_T + \sigma. \tag{9.170}$$

If we combine this with (9.160) and (9.167), we obtain

$$u_\sigma = \sigma - T\frac{d\sigma}{dT}. \tag{9.171}$$

The equation for the total internal energy of a surface, (9.163), then assumes the form:

$$U = \left(\sigma - T\frac{d\sigma}{dT}\right)\mathfrak{S}. \tag{9.172}$$

9.7.4. The area specific heat capacity of a surface layer, $c_\sigma$, is determined, according to (5.99), by the obvious relation

$$c_\sigma = T\left(\frac{\partial s_\sigma}{\partial T}\right)_{\mathfrak{S}}. \tag{9.173}$$

Using (9.169), we can write (9.173) as

$$c_\sigma = -T\frac{d^2\sigma}{dT^2}. \tag{9.174}$$

9.7.5. From relation (3.9)

$$F = U - TS$$

and relation (3.59)

$$\Phi^* = U + pV + \xi W - TS,$$

which for the given system can be written as

$$\Phi^* = U - \sigma\mathfrak{S} - TS, \tag{9.175}$$

with due regard for (9.169) and (9.172), it follows, respectively, that

$$F = \sigma\mathfrak{S} \tag{9.176}$$

and

$$\Phi^* = 0. \tag{9.177}$$

Hence, we see that the area specific values of $F$ and $\Phi^*$ are, respectively,

$$f_\sigma = \sigma \tag{9.178}$$

and

$$\varphi^* = 0. \tag{9.179}$$

We are not surprised at (9.179) since the mass of the surface layer is zero.

9.7.6. If we now turn to an ordinary three-dimensional system composed of a pure substance, the combined equation of the first and second laws of thermodynamics for such a system (1.30), in which surface effects are taken into account, is written as

$$T\,dS = dU + p\,dV - [\sigma[d\mathfrak{S}.$$

As to the thermodynamic properties of such a system, the relations for $U$, $H$, $F$, $\Phi$, $S$, and the heat capacities of the system are determined by the obvious relations reflecting the additivity of these quantities:

$$U = uG + \left(\sigma - T\frac{d\sigma}{dT}\right)\mathfrak{S}, \qquad (9.180)$$

$$H = hG + \left(\sigma - T\frac{d\sigma}{dT}\right)\mathfrak{S}, \qquad (9.181)$$

$$F = fG + \sigma\mathfrak{S}, \qquad (9.182)$$

$$\Phi = \varphi G, \qquad (9.183)$$

$$S = sG - \frac{d\sigma}{dT}\mathfrak{S}, \qquad (9.184)$$

$$C_p = c_pG - T\frac{d^2\sigma}{dT^2}\mathfrak{S}, \qquad (9.185)$$

$$C_v = c_vG - T\frac{d^2\sigma}{dT^2}\mathfrak{S}, \qquad (9.186)$$

where $G$ is the mass of the substance in the system. Obviously, when the ratio of the surface area of a liquid to its volume is small, the contribution of the surface of the liquid to the thermodynamic functions of the liquid is negligible.

## 9.8 Radiation in a Cavity as a Thermodynamic System

9.8.1. Equilibrium electromagnetic radiation in a closed cavity (photon gas) is a simple system performing only work of expansion. The only difference between the thermodynamic description of this system and that of usual simple systems is the specific character of the equation of state. In this connection we will briefly discuss the differential equations of the thermodynamics of such systems.

9.8.2. Electrodynamics uses the notion of radiation density $u_v$, which is defined as the amount of radiation energy per unit volume

$$u_v = U/V, \qquad (9.187)$$

where $U$ is the total radiation energy in the given cavity, and $V$ is the cavity volume. We know from electrodynamics that $u_v$ is a function of the temperature alone and is independent of volume. Hence, from (9.187) written as

$$U = u_vV,$$

it is clear that

$$\left(\frac{\partial U}{\partial V}\right)_T = u_v. \qquad (9.188)$$

Combining this with (5.2), we find that

$$u_v = T\left(\frac{\partial p}{\partial T}\right)_v - p. \qquad (9.189)$$

It is known from electrodynamics that electromagnetic radiation exerts pressure on a surface, which either reflects or absorbs the radiation. The radiation pressure and radiation density are uniquely related in the following manner:

$$p = u_v/3. \tag{9.190}$$

Taking this into account, we can transform (9.189) to

$$u_v = \frac{T}{3}\frac{du_v}{dT} - \frac{u_r}{3} \tag{9.191}$$

(since $u_v$ depends on the temperature alone, the derivative of $u_v$ with respect to $T$ is total).

Solving this differential equation, we obtain

$$u_v = aT^4, \tag{9.192}$$

where $a$ is a constant. This equation relates the radiation density to the temperature and is known as the *Stefan-Boltzmann law*.

Substituting (9.192) into (9.187), we obtain the relation for the total radiation energy in a volume $V$:

$$U = aT^4V. \tag{9.193}$$

Combining (9.190) with (9.192), we arrive at the following relation between radiation pressure and temperature:

$$p = \frac{a}{3}T^4. \tag{9.194}$$

This equation can be considered as the equation of state for a photon gas. We see that in a photon gas an isobar is an isotherm.

9.8.3. The Maxwell equations for the system under consideration are written in their usual form, relations (4.1b) through (4.4b).

For one, from (4.3b)

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$$

with due regard for (9.194), we see that

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{4}{3}aT^3, \tag{9.195}$$

whence it is obvious that

$$S(V, T) = \frac{4}{3}aT^3V \tag{9.196}$$

is the entropy of a photon gas in volume $V$; obviously, at $V = 0$ (i.e. when there is no system that contains the photon gas) the entropy equals zero.

From (9.196) we see that the volume specific entropy of the radiation is

$$s_v(T) = \frac{4}{3} aT^3, \qquad (9.197)$$

which obviously depends only on temperature.

9.8.4. The isobaric-isothermal potential, defined by the general formula (3.13)

$$\Phi = U + pV - TS,$$

proves to be zero for a photon gas: taking into account (9.193), (9.194), and (9.196), from (3.13) we obtain

$$\Phi = 0. \qquad (9.198)$$

This also implies that the chemical potential of a photon gas is zero.

9.8.5. The volume specific (constant-volume) heat capacity of a photon gas, $C_v$, is defined by the conventional relation

$$C_v = T\left(\frac{\partial s_v}{\partial T}\right)_v, \qquad (9.199)$$

which when combined with (9.197) yields

$$C_v = 4aT^3. \qquad (9.200)$$

As to the constant-pressure heat capacity of a photon gas, since, as we noted before, an isobar is also an isotherm for radiation and the heat capacity of an isothermal process is infinite, we find that for a photon gas $C_p = \infty$.

# Notation Index

## Latin Symbols

| | |
|---|---|
| $a$ | Thermodynamic sound velocity |
| $C_z$ | Heat capacity at $z = \text{const}$ |
| $c_z$ | Specific heat capacity at $z = \text{const}$ |
| $E$ | Electric field strength |
| $E$ | Young's modulus (Sec. 9.5) |
| $\mathscr{E}$ | Electromotive force |
| $F$ | Isochoric-isothermal potential |
| $\tilde{F}$ | Massieu function |
| $f$ | Specific isochoric-isothermal potential |
| $\tilde{f}$ | Specific Massieu function |
| $G$ | Mass |
| $g$ | Acceleration of free fall |
| $H$ | Enthalpy |
| $H$ | Magnetic field strength (Secs. 7.2, 9.2) |
| $\tilde{H}$ | Characteristic function of the variables $U$, $V$, and $G/T$ |
| $h$ | Specific enthalpy |
| $I$ | Characteristic function of variables $U$ and $p/T$ |
| $i$ | Specific value of the characteristic function $I$ |
| $j$ | Specific magnetization |
| $k$ | Adiabatic exponent |
| $L$ | Work |
| $L^*$ | Any type of work other than expansion work |
| $l$ | Specific work $L$ |
| $l$ | Length of a deformed rod (Sec. 9.5) |
| $l^*$ | Specific work $L^*$ |
| $\mathrm{M}$ | Mach number |
| $P$ | Electric dipole moment per unit volume of the dielectric (Sec. 9.3) |
| $Q$ | Amount of heat |
| $Q_p$ | Heat of isobaric-isothermal reaction |
| $Q_v$ | Heat of isochoric-isothermal reaction |
| $q$ | Specific amount of heat |
| $q$ | Heat of phase transition of superconductor from the superconducting state to the normal (Secs. 7.2, 9.2) |
| $R$ | Gas constant |
| $r$ | Heat of phase transition |
| $S$ | Entropy |
| $s$ | Specific entropy |
| $T$ | Thermodynamic temperature |
| $U$ | Internal energy |
| $\tilde{U}$ | Characteristic function of the variables $U$, $p/T$, and $\varphi/T$ |
| $u$ | Specific internal energy |
| $V$ | Volume |
| $v$ | Specific volume |
| $W$ | A generalized coordinate with the exception of volume |

| | |
|---|---|
| $w$ | Specific value of the generalized coordinate $W$ |
| $w$ | Flow velocity (Sec. 5.7) |
| $x$ | Degree of dryness of the two-phase system |
| $Y$ | Generalized coordinate |
| $y$ | Specific value of the generalized coordinate $Y$ |
| $Z$ | Charge of a reversible voltaic cell (Sec. 9.6) |
| $z$ | Height |

## German Symbols

| | |
|---|---|
| $\mathfrak{C}$ | Capacitance of a capacitor |
| $\mathfrak{M}$ | Torque |
| $\mathfrak{P}$ | Polarization of a dielectric |
| $\mathfrak{S}$ | Surface area |
| $\mathfrak{W}$ | Voltage across the plates of an electric capacitor |

## Greek Symbols

| | |
|---|---|
| $\alpha$ | Bulk thermal expansion coefficient |
| $\alpha$ | Dielectric susceptibility (Sec. 9.3) |
| $\alpha_l$ | Linear thermal expansion coefficient |
| $\beta_T$ | Coefficient of isothermal compressibility |
| $\beta_s$ | Coefficient of adiabatic compressibility |
| $\Gamma$ | Grand potential |
| $\tilde{\Gamma}$ | Cramers function |
| $\varepsilon$ | Permittivity of a dielectric (Sec. 9.3) |
| $\varepsilon$ | Strain (Sec. 9.5) |
| $\zeta$ | Generalized force |
| $\Lambda$ | Characteristic function of the variables $S$, $p$, and $\varphi$ |
| $\lambda$ | Integrating factor |
| $\mu$ | Joule-Thomson coefficient |
| $\mu$ | Poisson ratio (Sec. 9.5) |
| $\xi$ | Any generalized force with the exception of pressure |
| $\Xi$ | Characteristic function of the variables $S$, $V$ and $\varphi$ |
| $\rho$ | Density |
| $\Sigma$ | Area of the channel's cross-section |
| $\sigma$ | Surface tension |
| $\Phi$ | Isobaric-isothermal potential |
| $\tilde{\Phi}$ | Planck function |
| $\varphi$ | Chemical potential |
| $\tilde{\varphi}$ | Specific Planck function |
| $\chi$ | Specific magnetic susceptibility |
| $\Psi$ | Tensile (compressive) force |
| $\psi$ | Stress |
| $\Omega$ | Cross-sectional area of the deformed rod |
| $\omega$ | Twist angle |

## Subscripts

| | |
|---|---|
| $\sigma$ | Denotes values on the saturation line |

## Superscripts

| | |
|---|---|
| $*$ | Denotes quantities referring to complex thermodynamic systems |
| one-phase | Denotes quantities for one-phase region |
| two-phase | Denotes quantities for two-phase region |
| (1) and (2) | Denote quantities for two coexisting phases |
| $'$ | Denotes the liquid phase |
| $''$ | Denotes the vapor phase |

# Subject Index